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Fluorinated Polyhedral Oligomeric Silsesquioxanes (FluoroPOSS)

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15. SUBJECT TERMS

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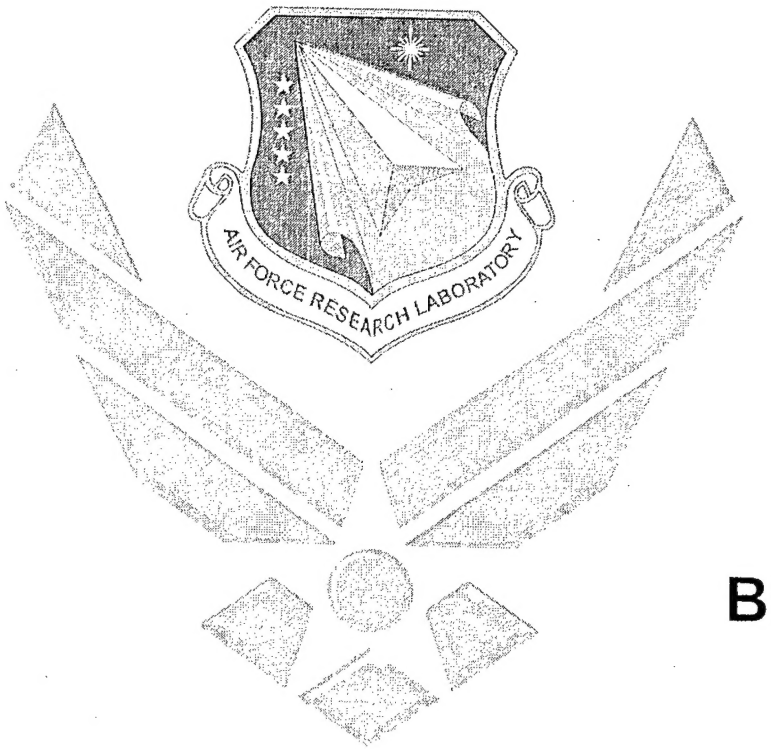
Fluorinated Polyhedral Oligomeric Silsesquioxanes (FluoroPOSS)



Silicones and Silicone-Modified Materials

April 1, 2004

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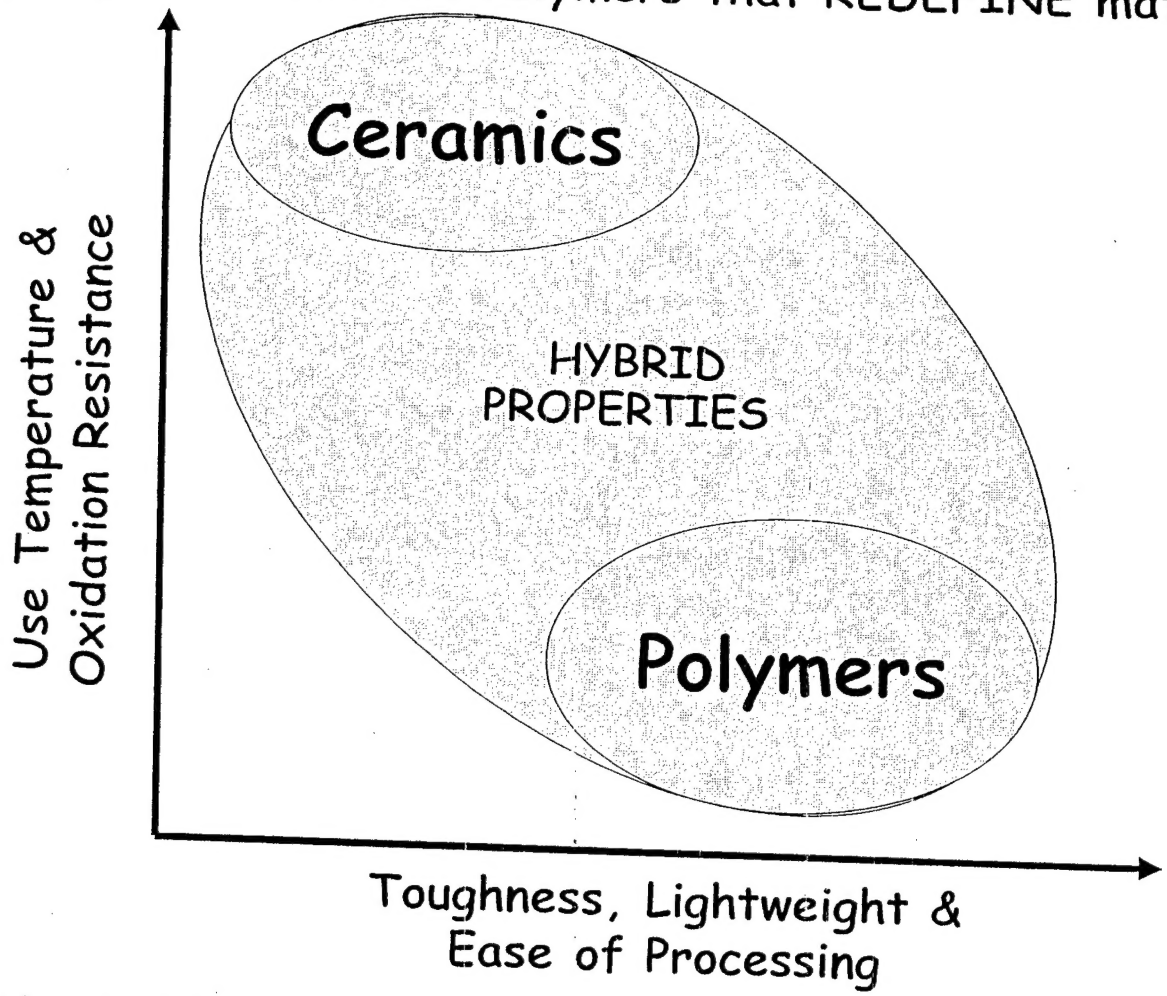
Hybrid Inorganic/Organic Polymers

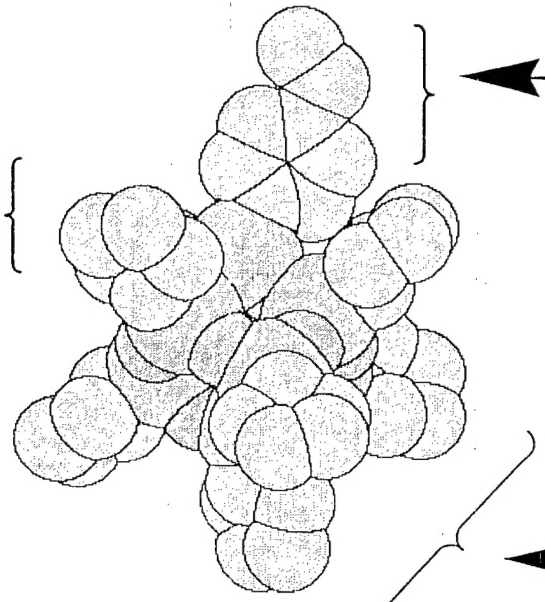
Goal: Develop High Performance Polymers that REDEFINE material properties



PAS-03-061

- Hybrid plastics bridge the differences between ceramics and polymers

Anatomy of a POSS Nanostructure



Nonreactive organic (R) groups for solubilization and compatibilization.

Nanoscopic in size with an Si-Si distance of 0.5 nm and a R-R distance of 1.5 nm.

May possess one or more functional groups suitable for polymerization or grafting.

Thermally and chemically robust hybrid (organic-inorganic) framework.

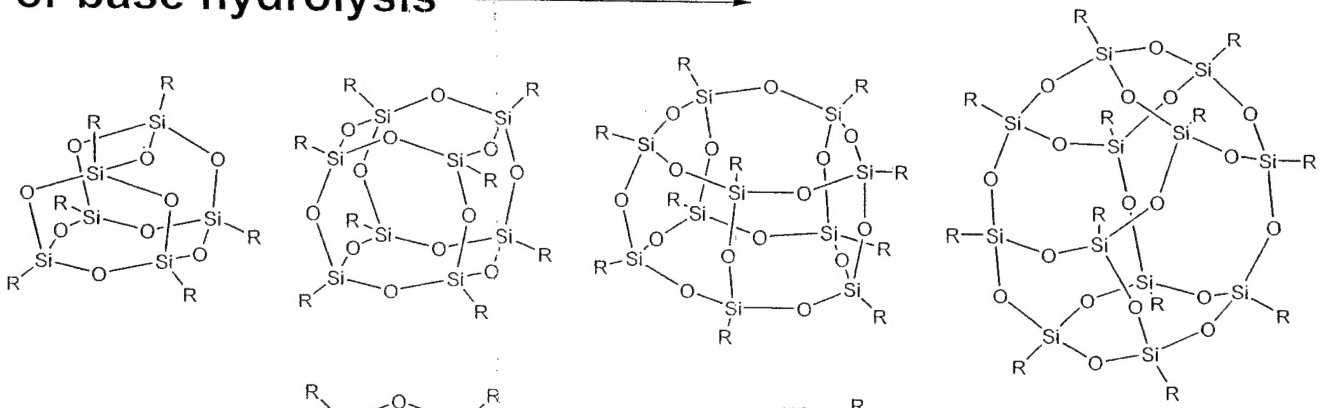
Precise three-dimensional structure for molecular level reinforcement of polymer segments and coils.

PAS-03-061

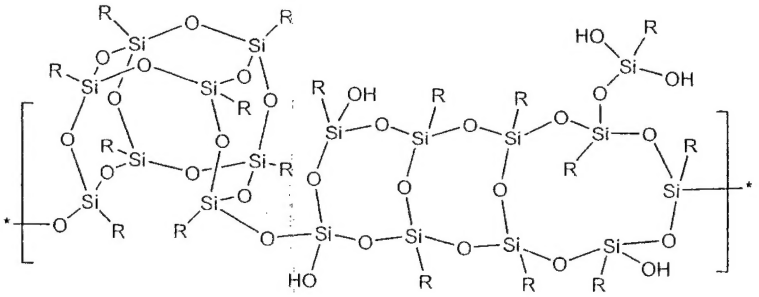
POSS Synthesis

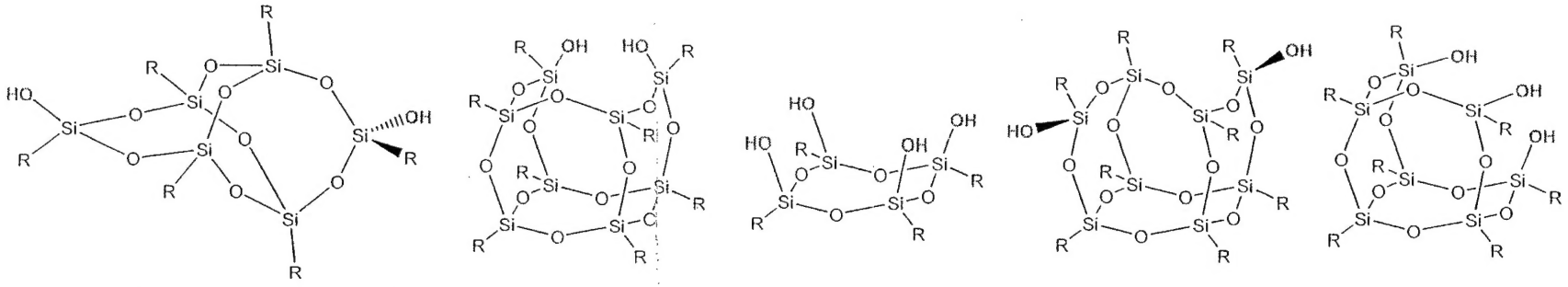
$RSiX_3$ acid or base hydrolysis ⟶

Completely condensed



Resin



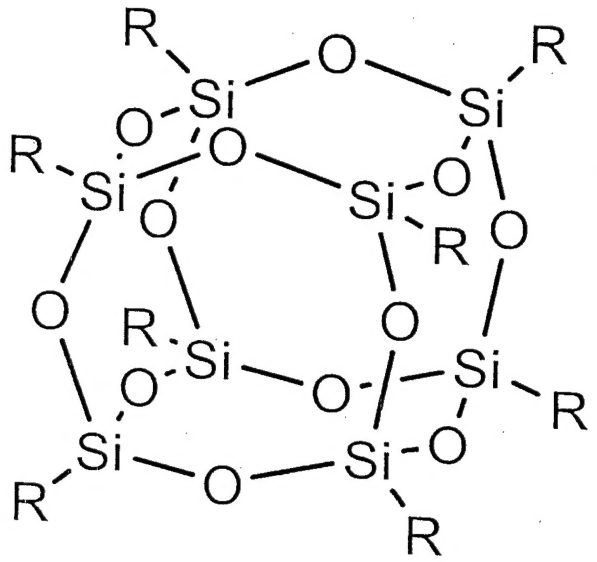


Incompletely condensed

Brown, Feher, AFRL, Hybrid Plastics

FluoroPOSS Synthesis

R_fSiX_3 $\xrightarrow[\text{solvent}]{KOH / H_2O}$



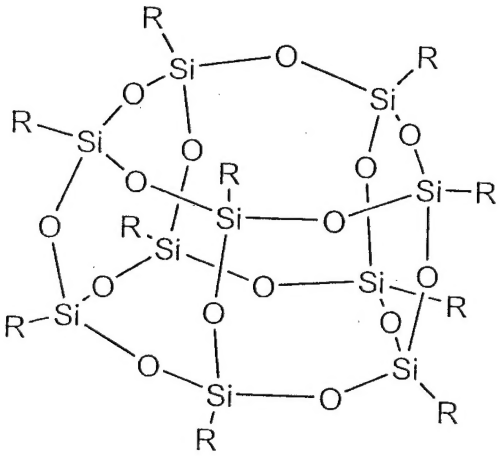
$R_{f8}T_8$

X = -OMe, -OEt

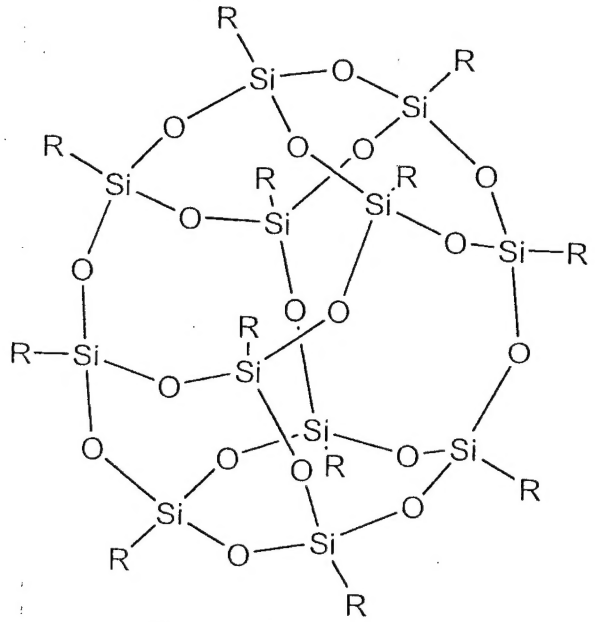
R_f = $-CH_2CH_2CF_3$, $-CH_2CH_2(CF_2)_3CF_3$,
$-CH_2CH_2(CF_2)_5CF_3$, $-CH_2CH_2(CF_2)_7CF_3$

Fluoropropyl$_n$T$_n$

R = -$CH_2CH_2CF_3$



T_{10} (~11%)



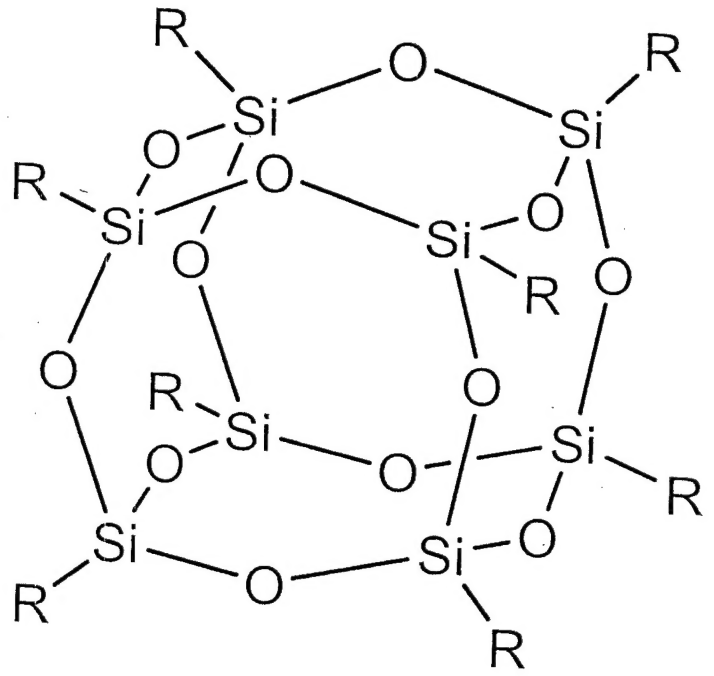
T_{12} (~89%)

Fluorodecyl$_8$T$_8$

$R = -CH_2CH_2(CF_2)_7CF_3$

$M_W = 3993.54$ g/mol

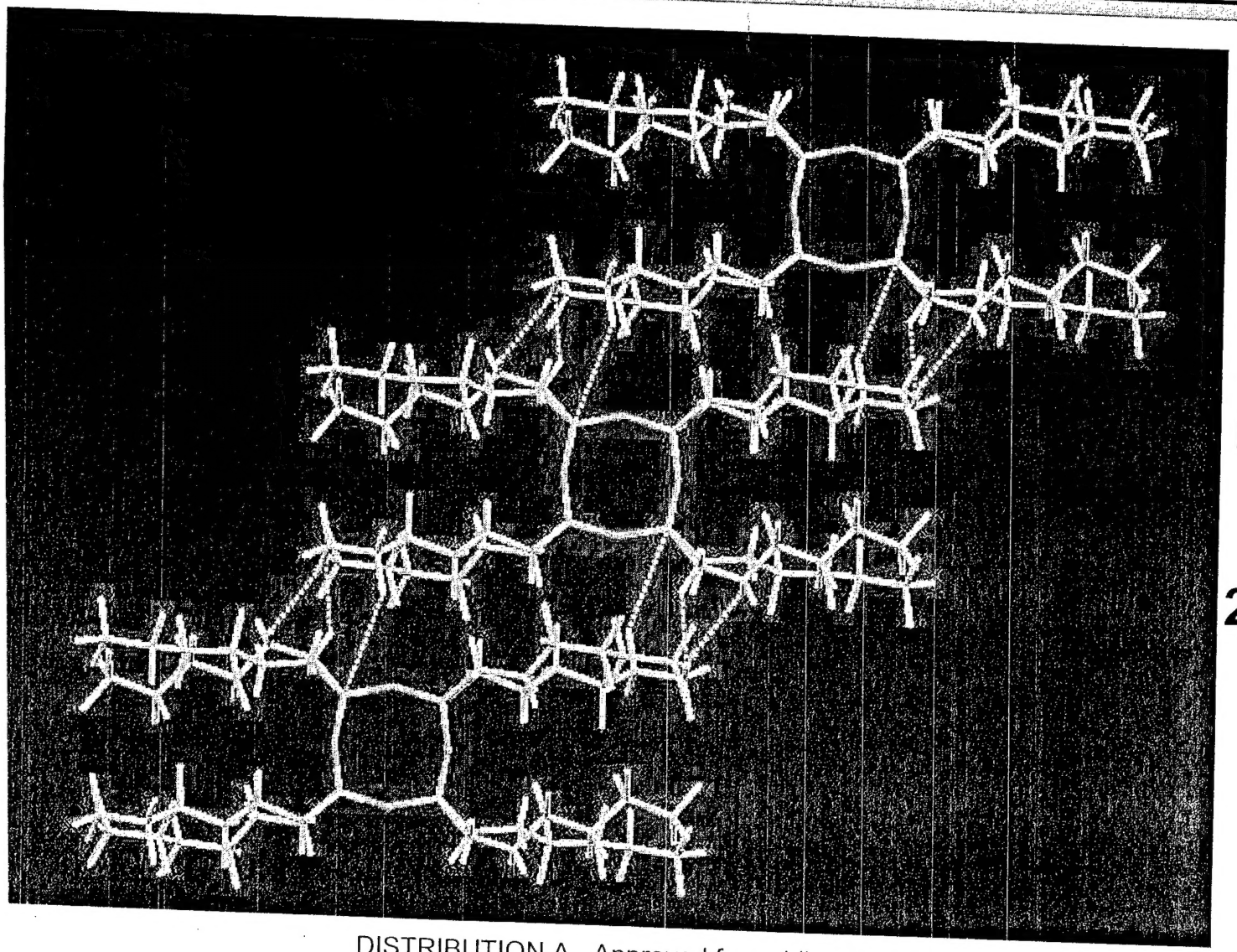
$\rho = 2.058$ g/mL



T_8

($-C_{10}H_4F_{17}$ = Fluorodecyl)

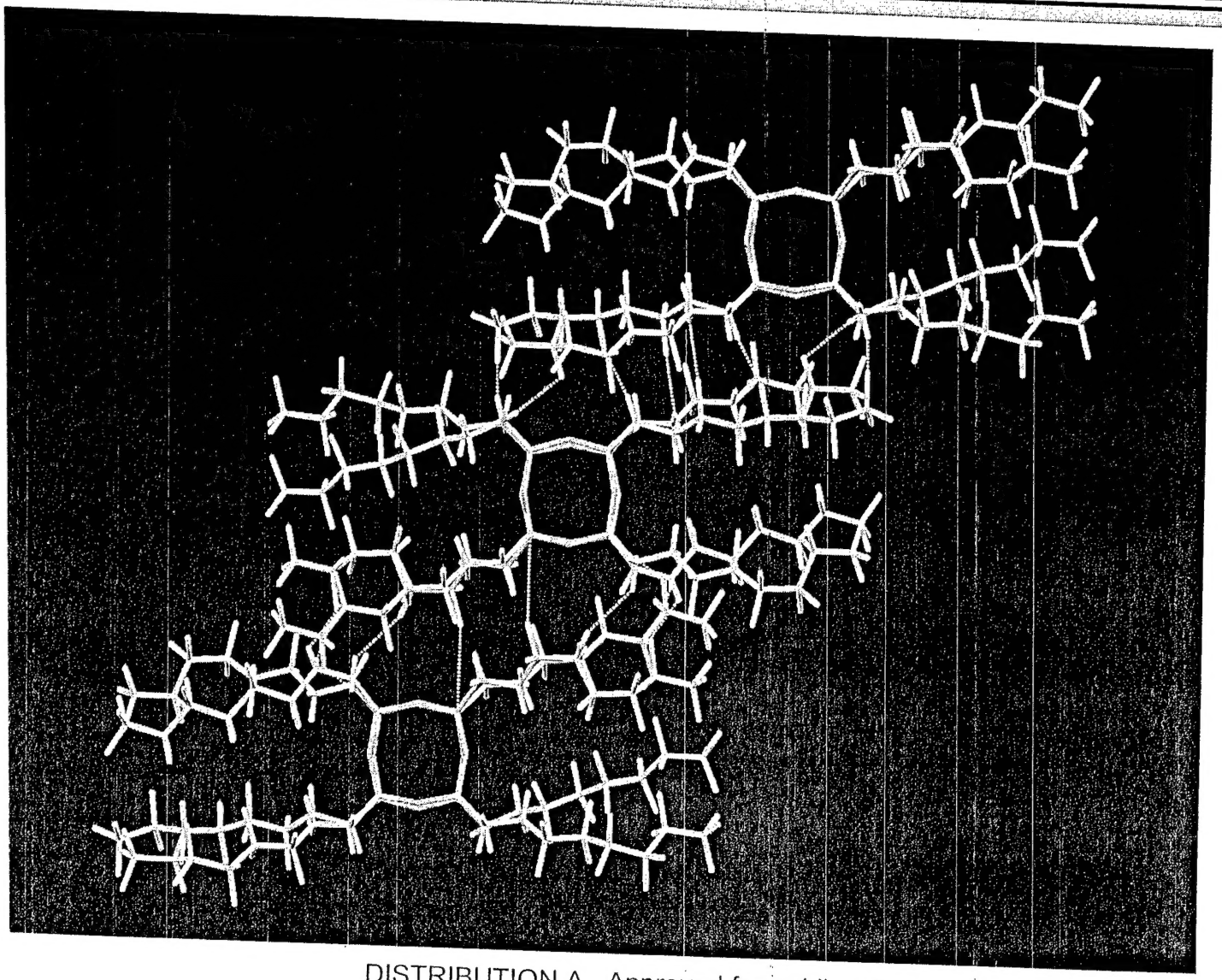
Fluorohexyl$_8$T$_8$



ρ = 1.98 g/mL

M_w = 2393.33 g/mol

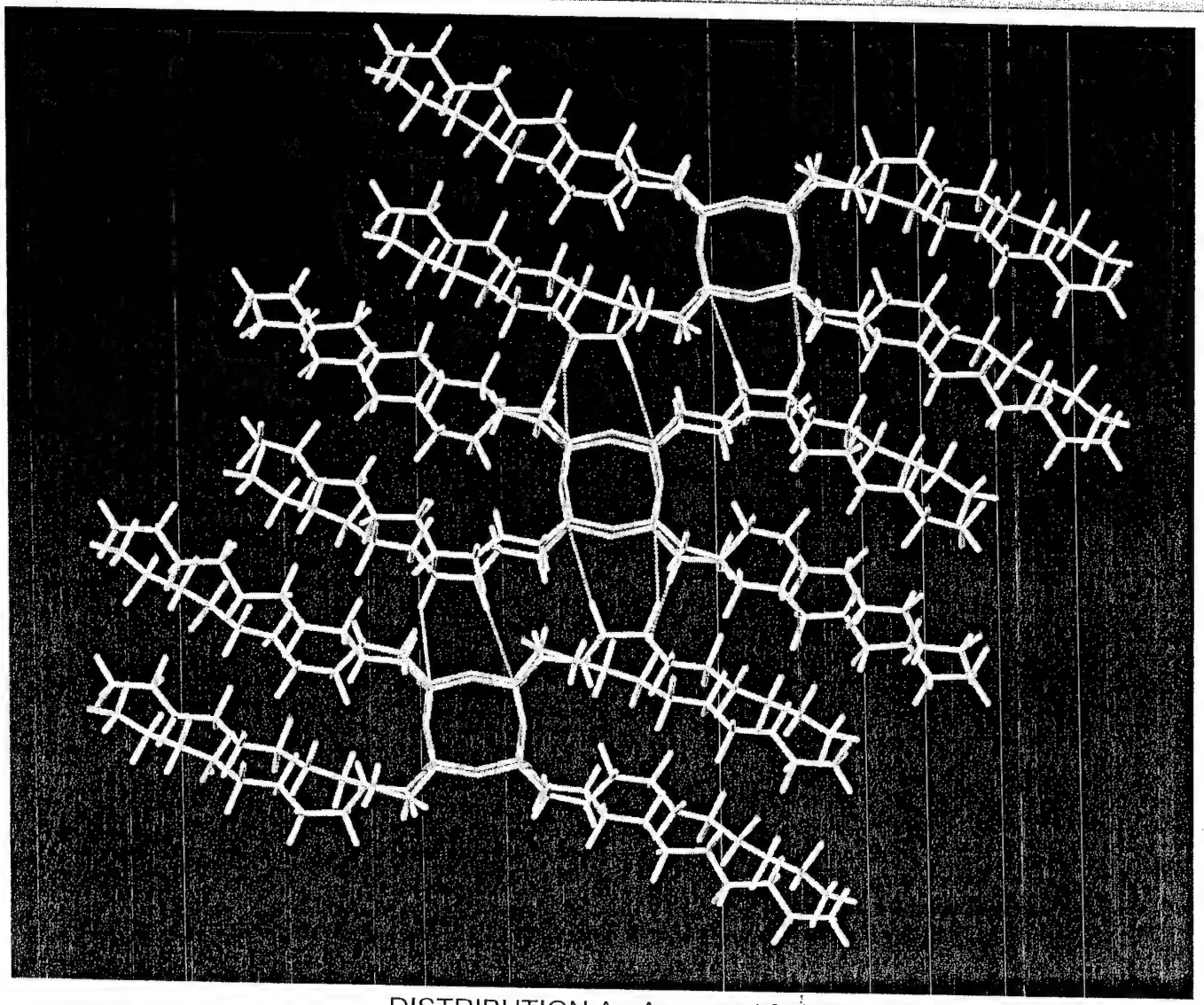
Fluorooctyl$_8$T$_8$



ρ = 2.05 g/mL

M_w = 3193.45 g/mol

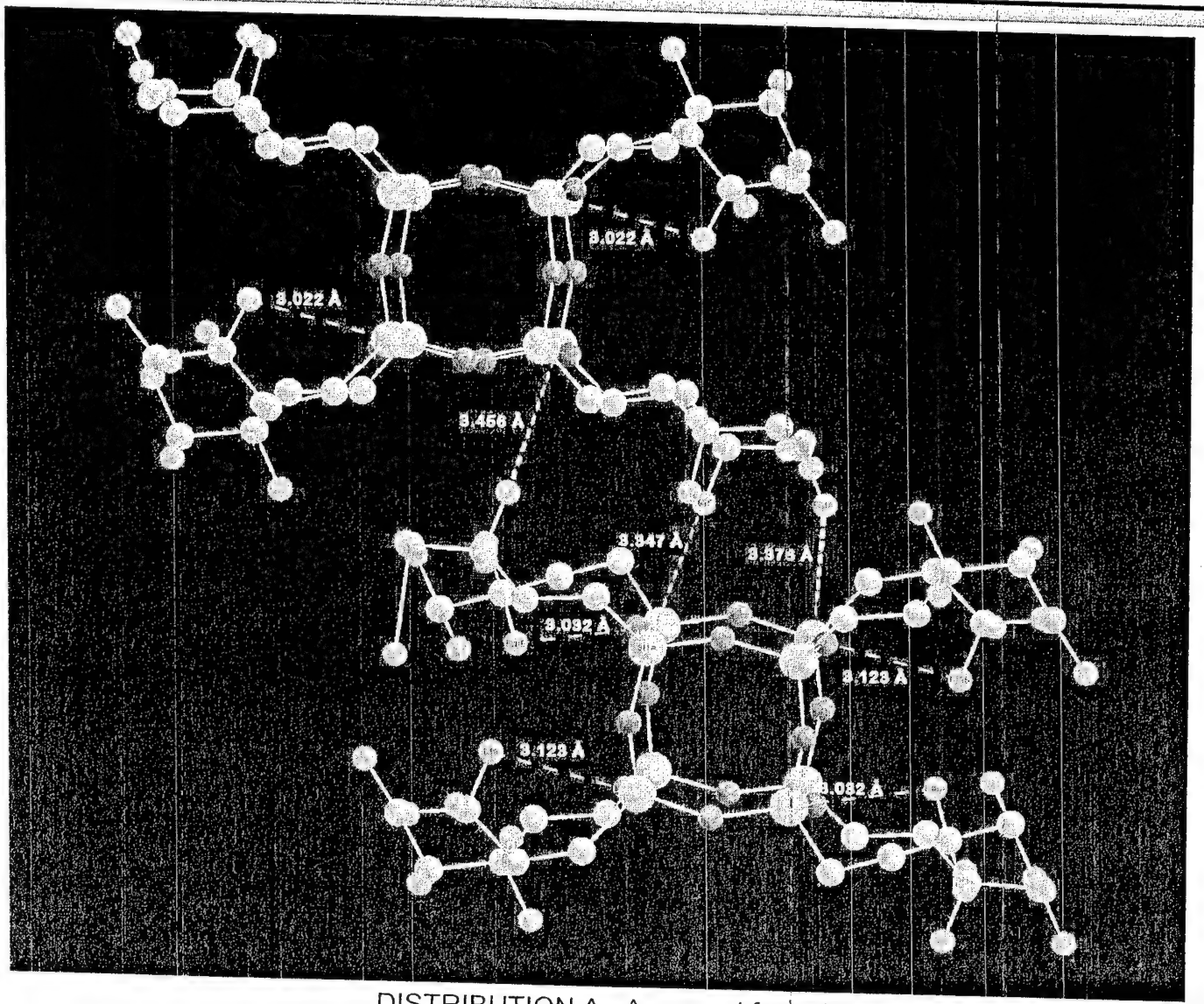
Fluorodecyl$_8$T$_8$



ρ = 2.06 g/mL

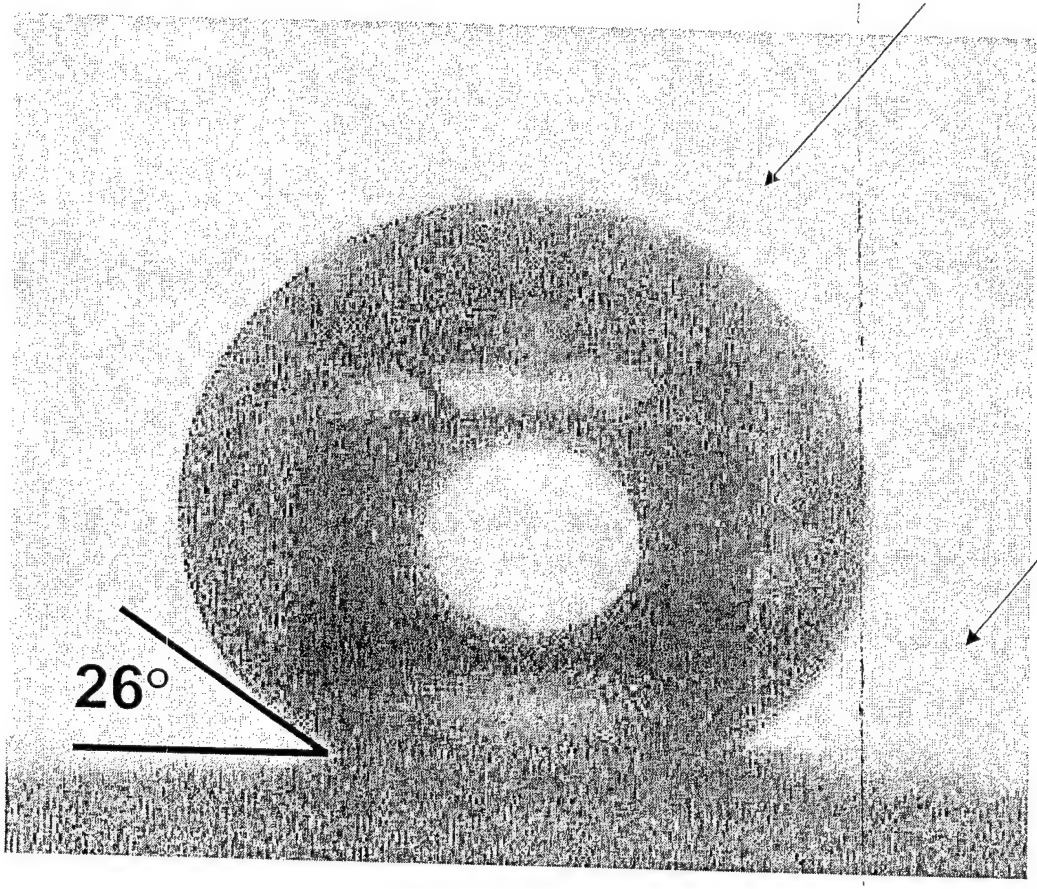
M_w = 3993.54 g/mol

Fluorodecyl$_8$T$_8$



Inter- and intra-molecular Si-F contacts affect crystal packing

Contact Angle of Water on Fluorodecyl POSS Surface



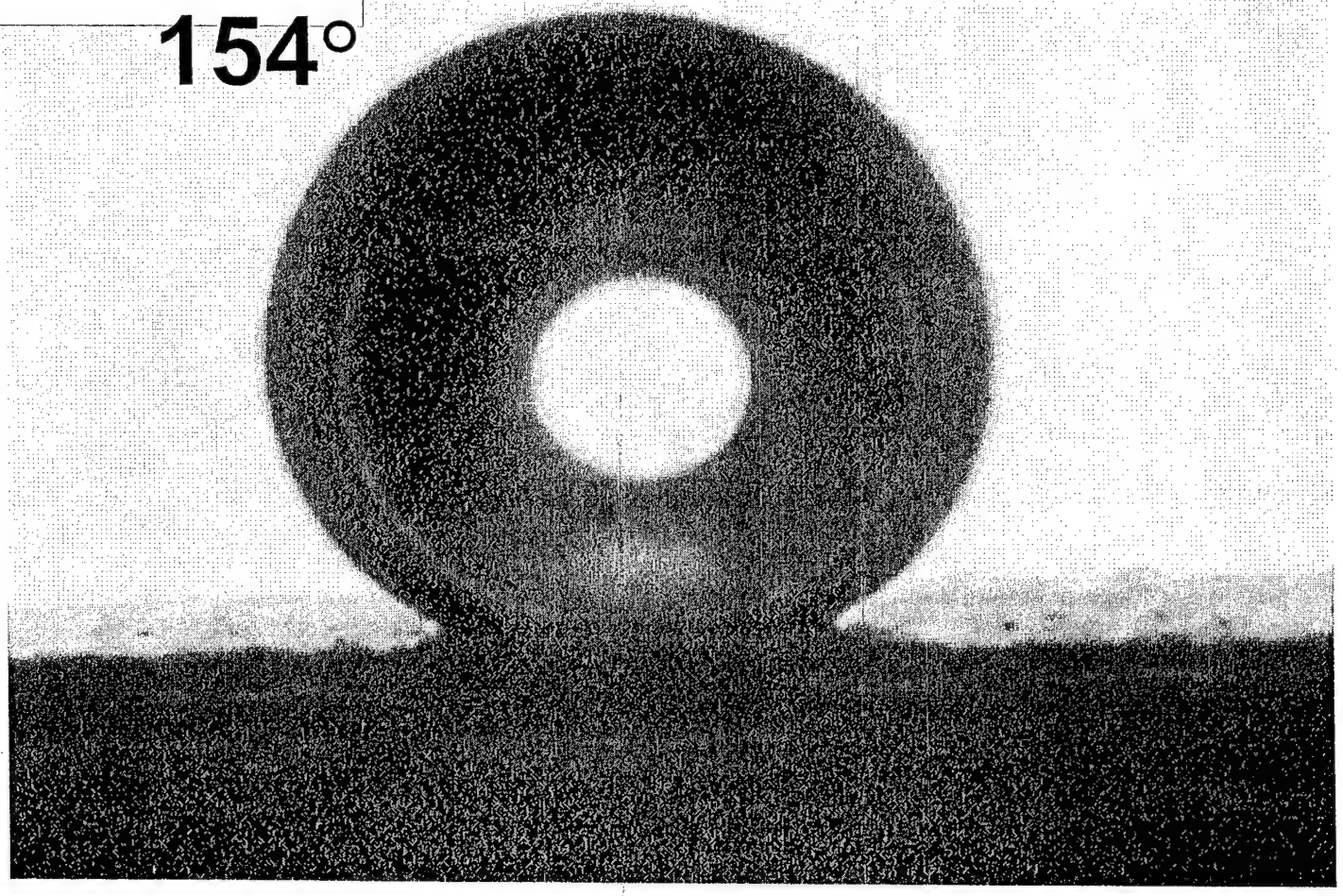
POSS Coated Surface

-Anti Icing surfaces
-Low Friction Surfaces

40° Higher than PTFE

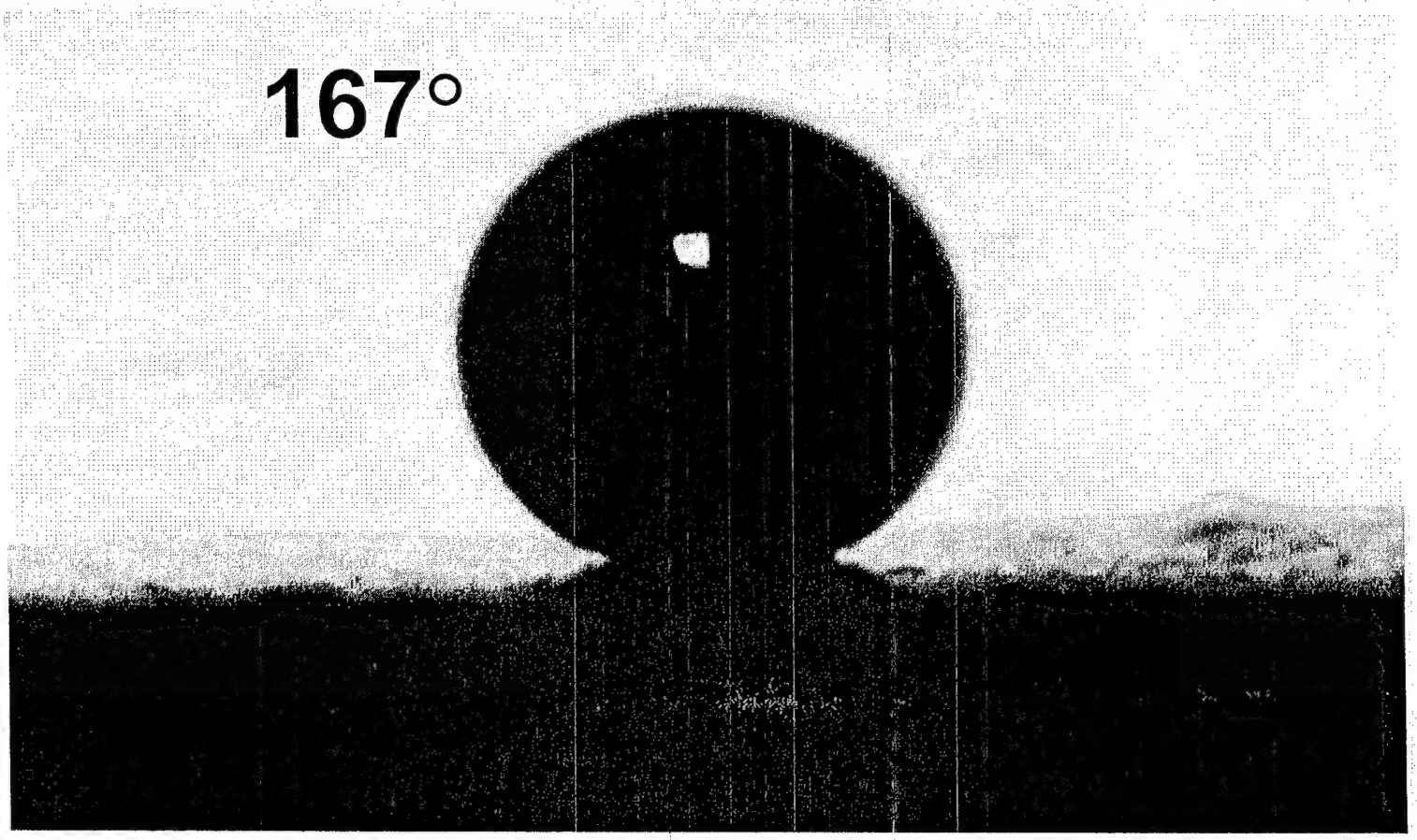
Contact Angle of Water on Fluorodecyl POSS Surface

154°

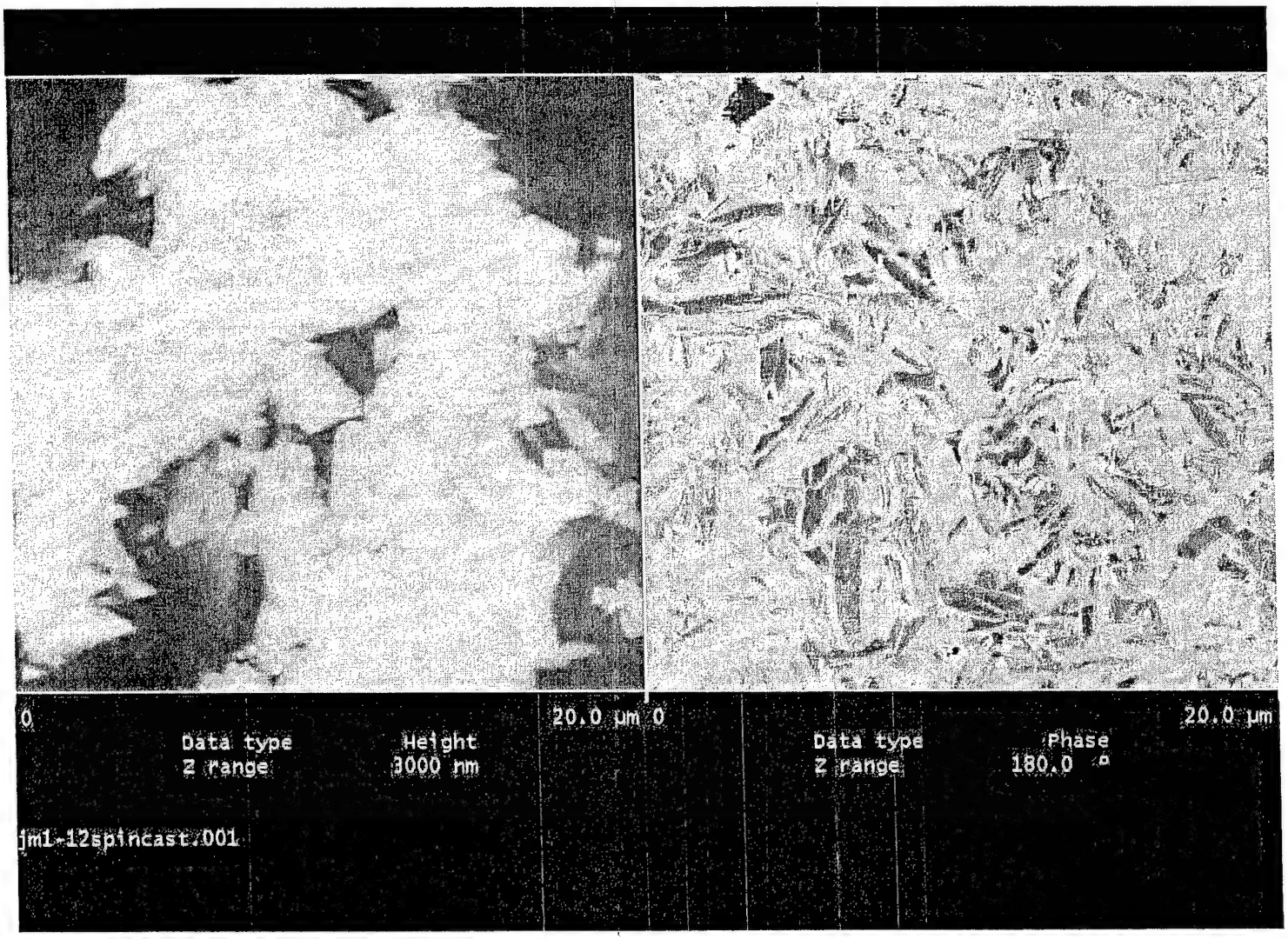


40° Higher than PTFE

Contact Angle of Mercury on Fluorodecyl POSS Surface



AFM Image of Spin-Cast Fluorodecyl$_8$T$_8$ Surface

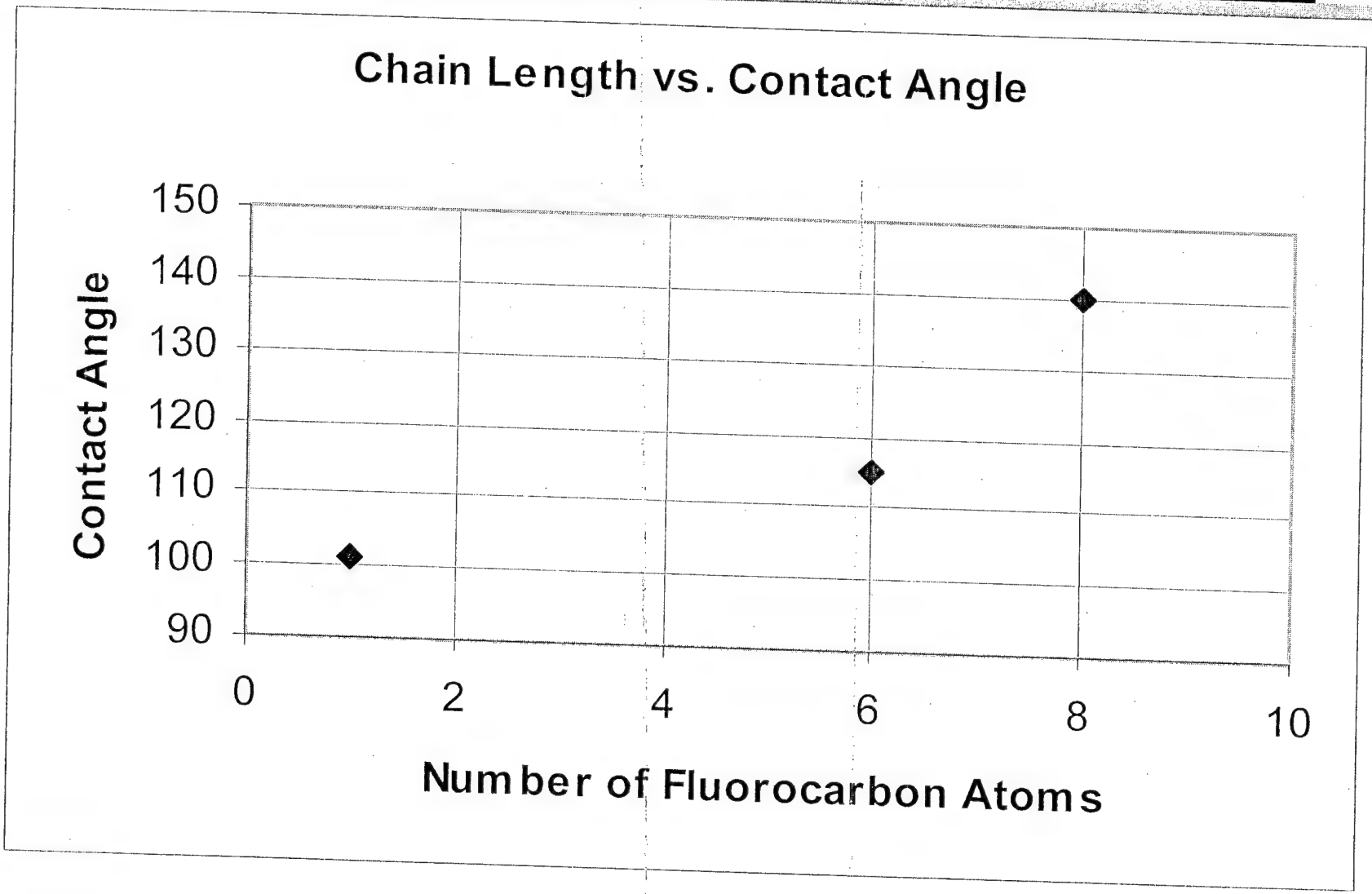


Surface Energy of Fluorosiloxanes

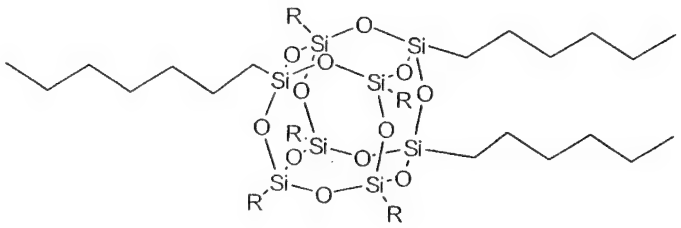
Polymer	Surface Energy (mJ/m^2)
Poly(methylheptadecafluorodecylsiloxane)	7.0
Poly(methylnonafluorohexylsiloxane)	9.5
Poly(methyltrifluoropropylsiloxane)	13.6
Poly(dimethylsiloxane) (PDMS)	22.8
Poly(tetrafluoroethylene) (PTFE)	19.1

Maxson, M. T.; Norris, A. W.; Owen, M. J. "Fluorosilicones" In "Modern Fluoropolymers"; Scheirs, J. Ed.; J. Wiley & Sons: New York, 1997, pp 359-372.

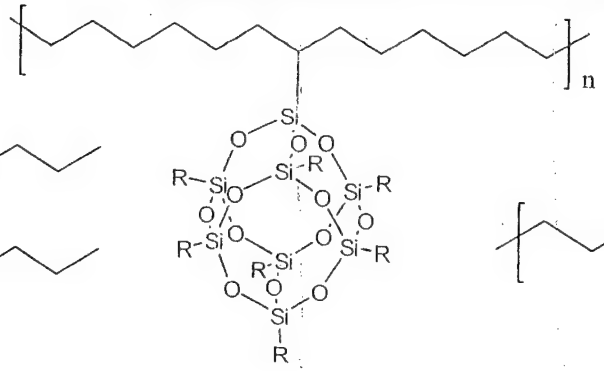
Contact Angle and Chain Length



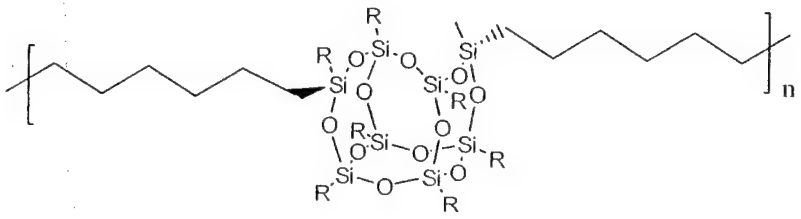
POSS Polymer Incorporation



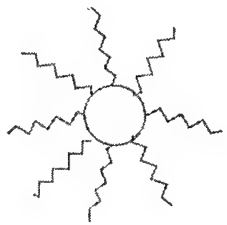
Cross-linker



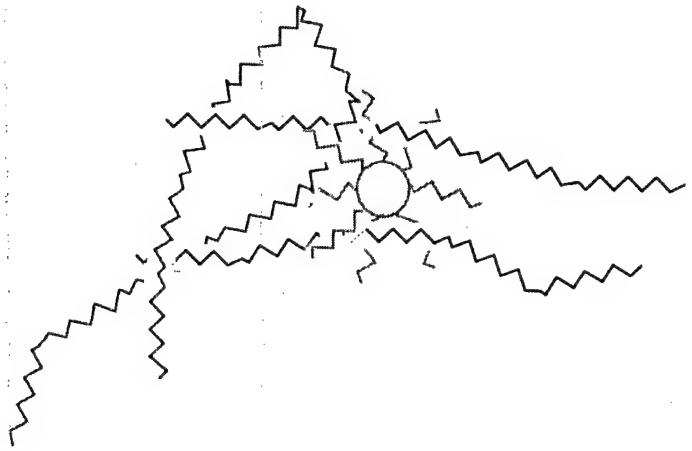
POSS Pendant



Bead Copolymer

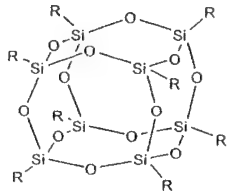


POSS Blending

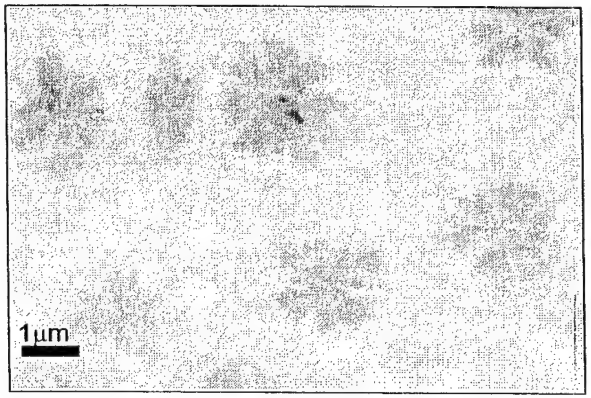


Importance of R groups: Affect compatibility with polymer matrix

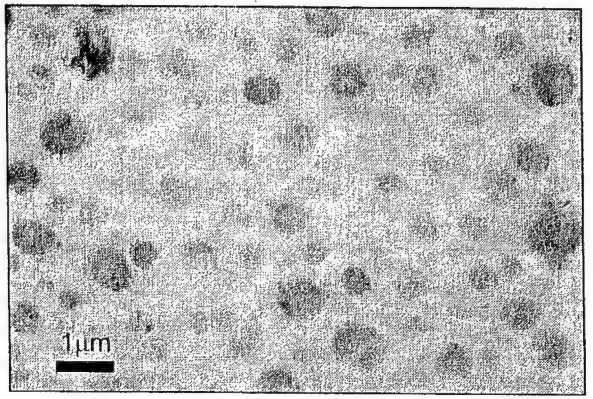
50 Wt % POSS Blends in 2 Million MW PS



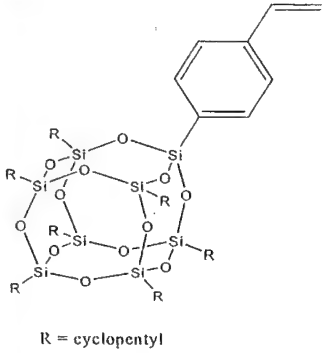
Cp_8T_8



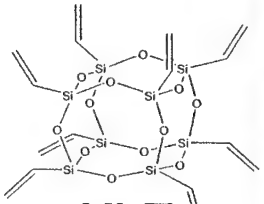
Domain Formation



Partial Compatibility

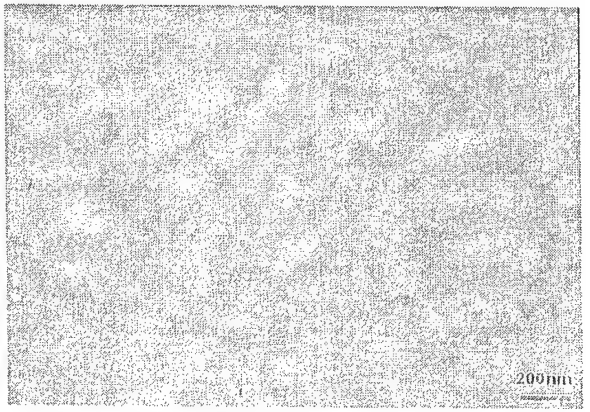


$Cp_7T_8Styryl$

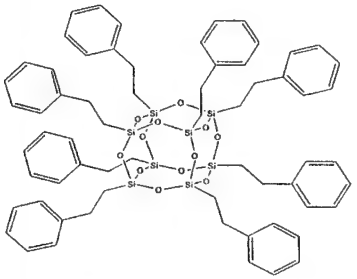


Vi_8T_8

Immiscible POSS Crystallites



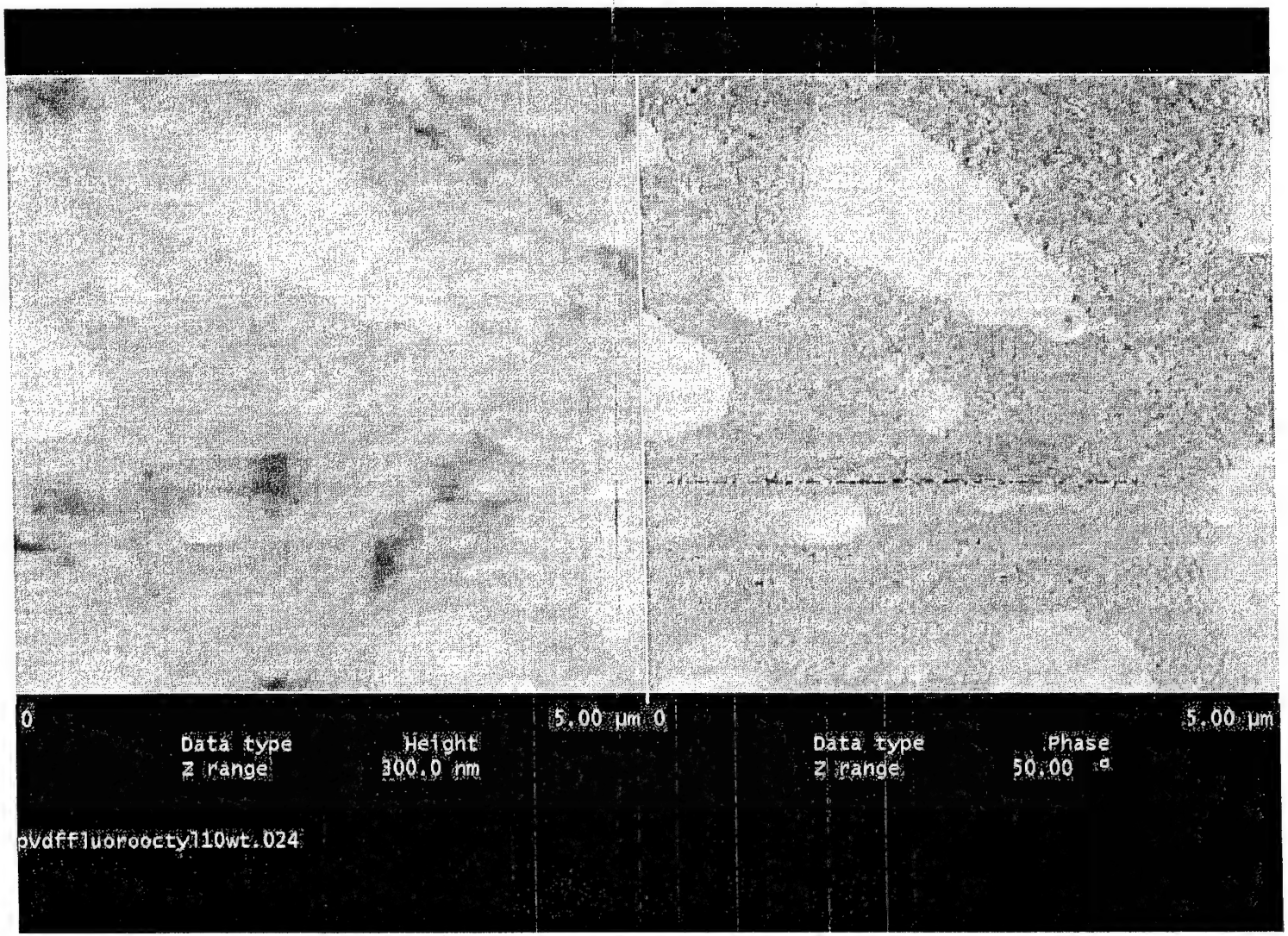
Complete Compatibility



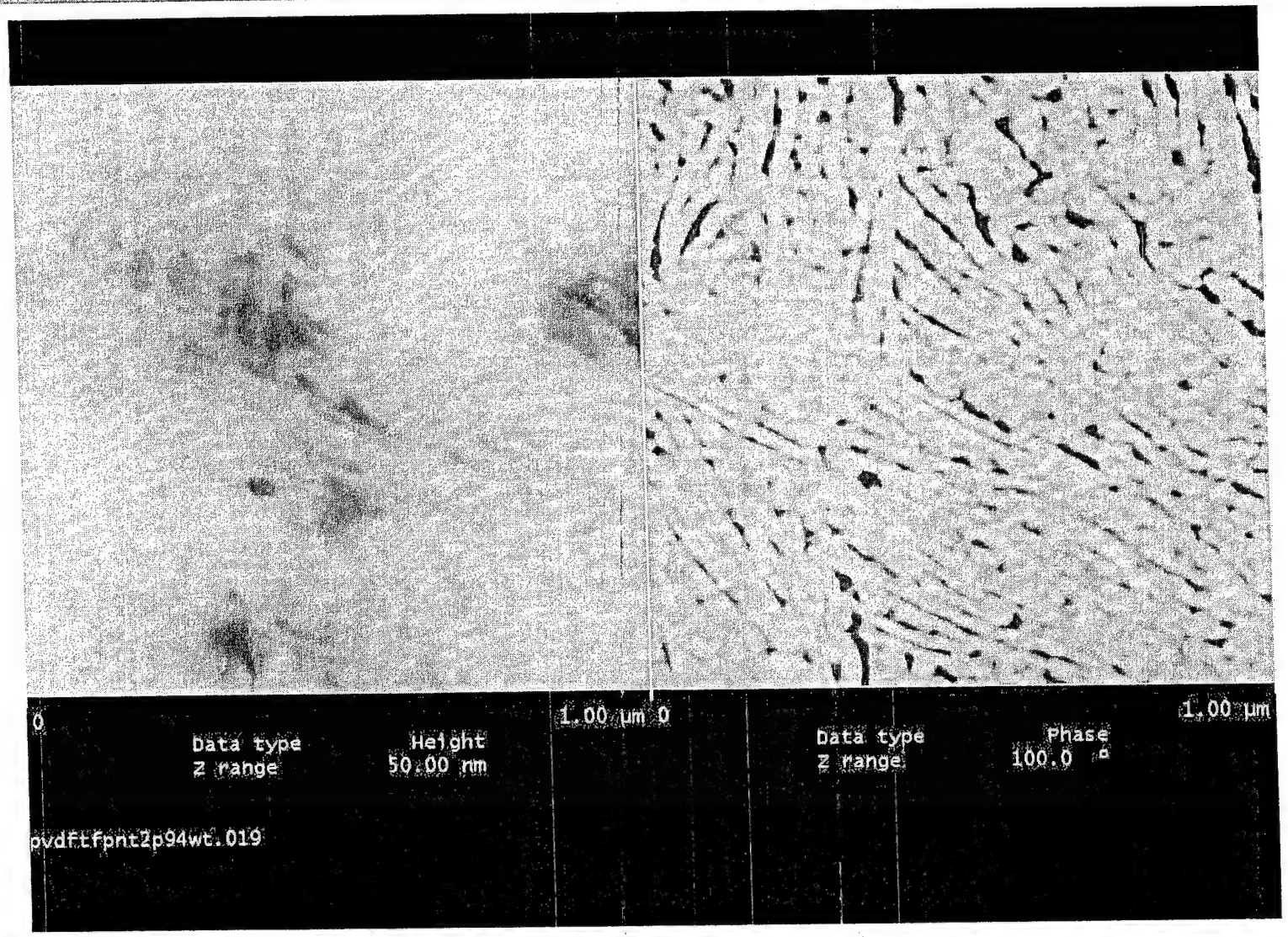
$Phenethyl_8T_8$

Blanski, et al., *Polymer Preprints*, **2000**. 41(1): p. 585.

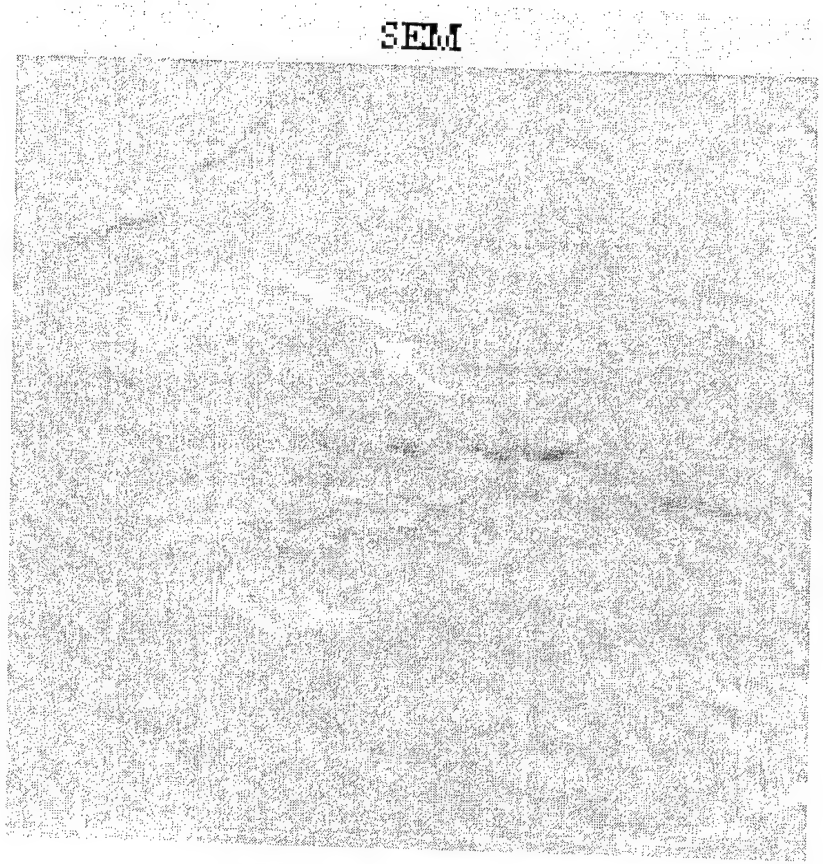
PVDF/Fluorooctyl$_8$T$_8$ POSS



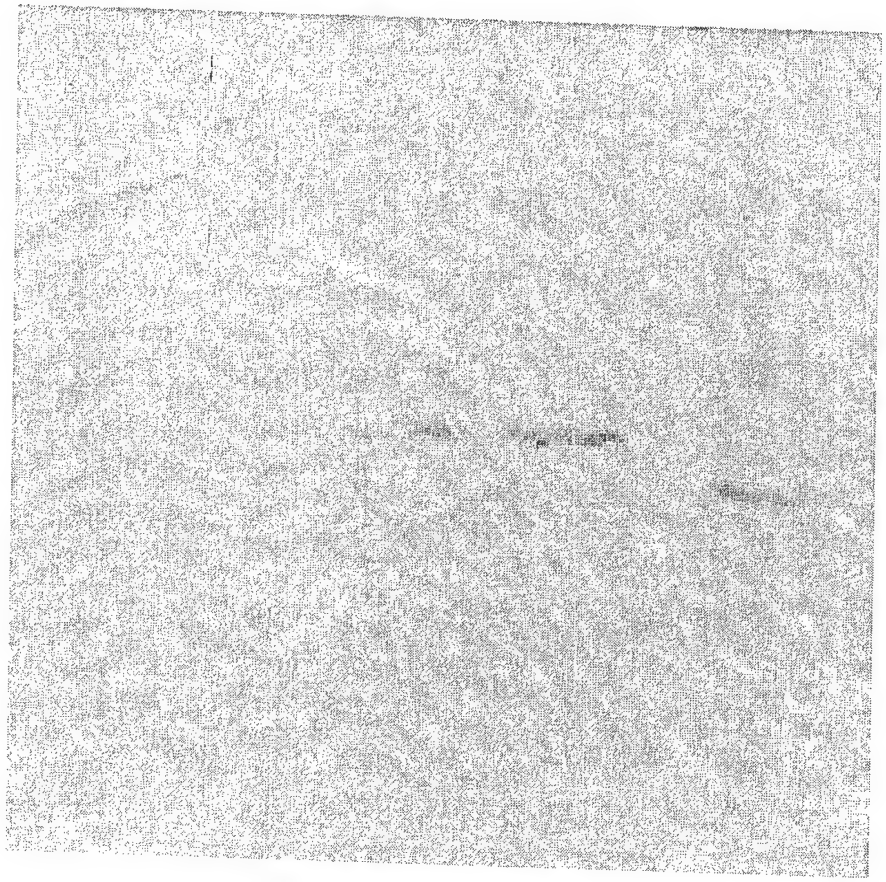
PVDF/Fluoropropyl$_n$T$_n$ POSS



PVDF/Fluoropropyl$_n$T$_n$ POSS



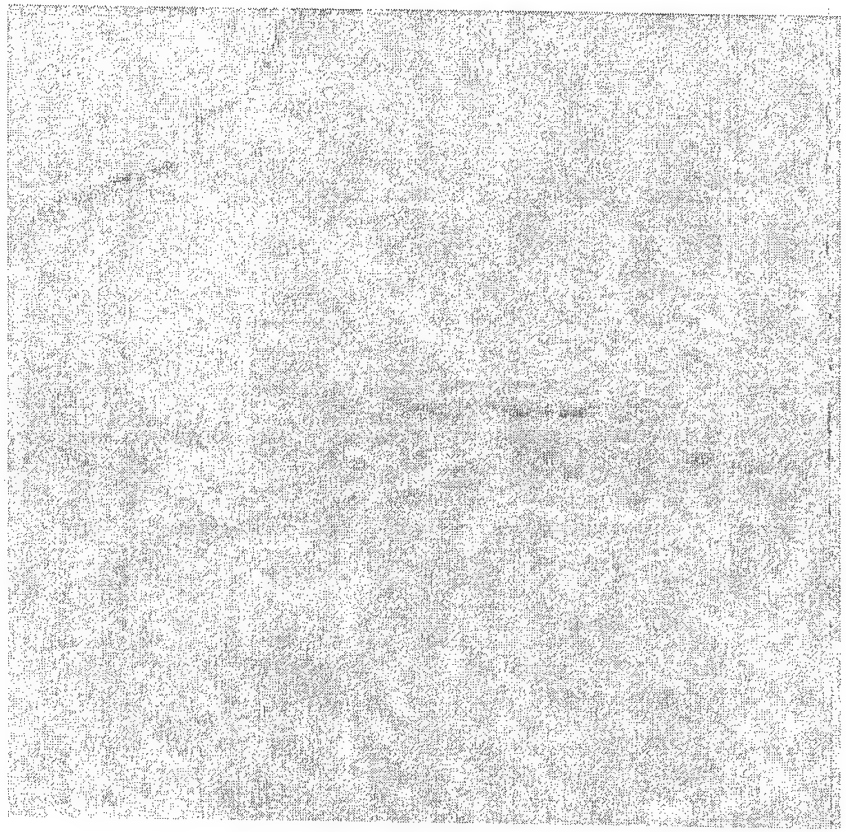
SEM Image



Carbon Map

SEM Image taken on cross-section of ¼ inch thick sample bar.

PVDF/Fluoropropyl$_n$T$_n$ POSS



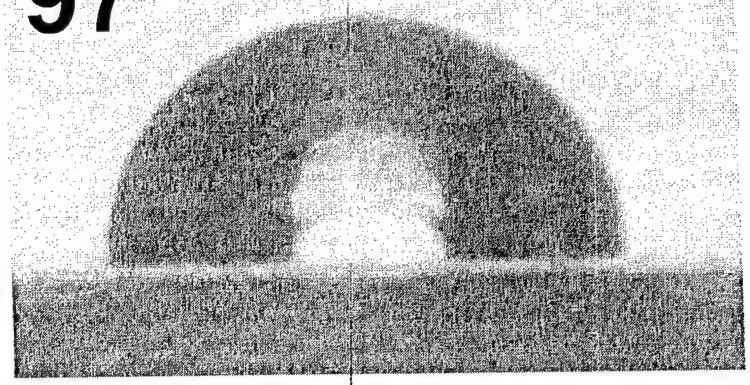
Fluorine Map

Silicon Map

Silicon map shows reasonable dispersion of POSS in polymer.

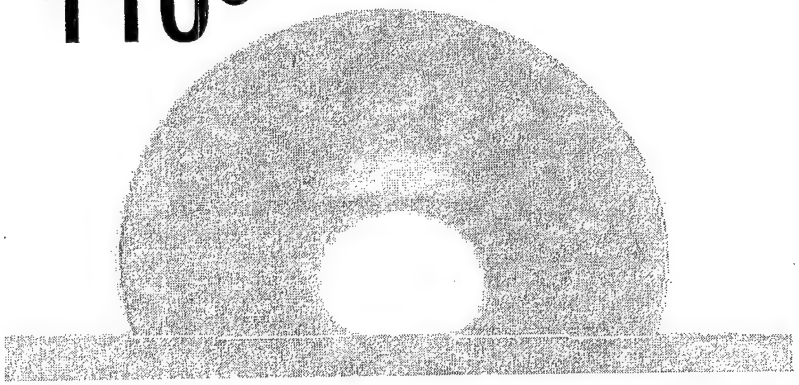
Fluorinated Ethylene/Propylene

97°



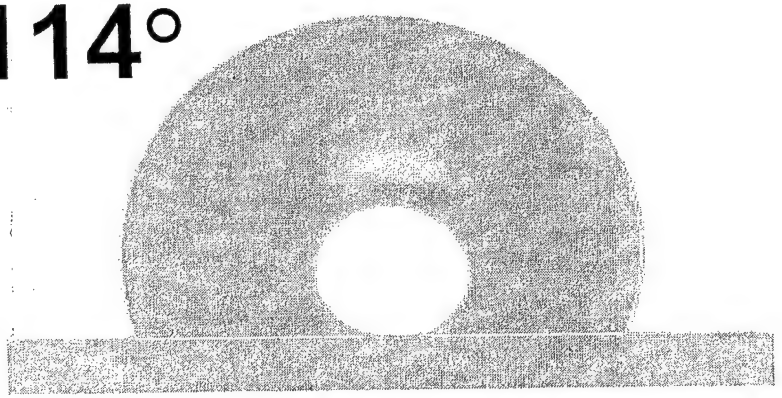
FEP

110°



15% FO_8T_8

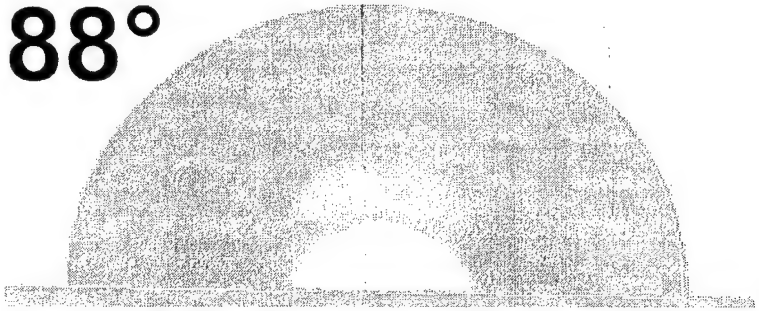
114°



15% FD_8T_8

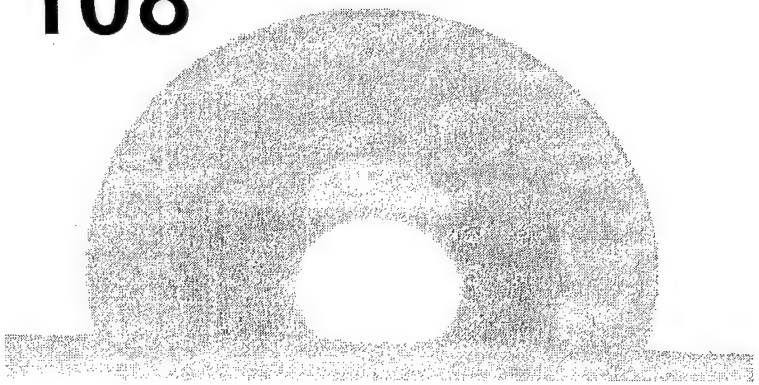
Poly(chlorotrifluoroethylene)

88°



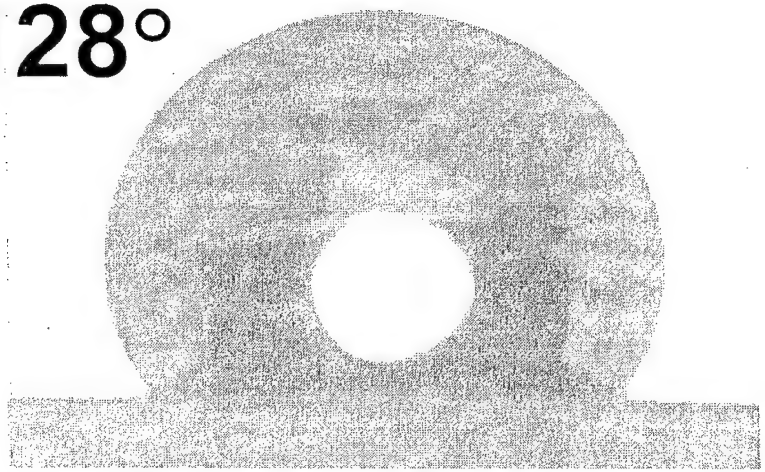
PCTFE

108°



10% FO_8T_8

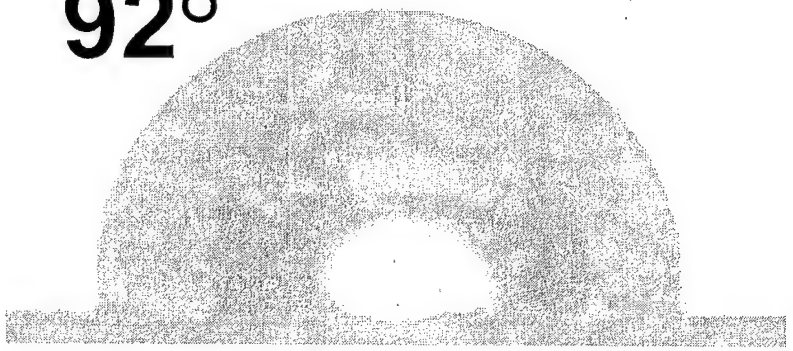
128°



10% FD_8T_8

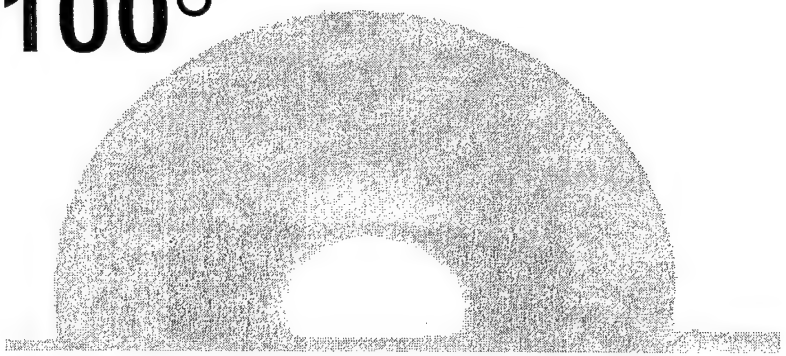
Amorphous FEP

92°



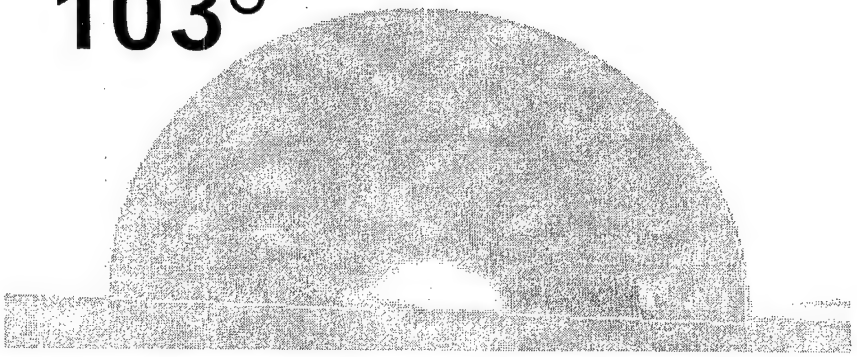
AFEP

100°



AFEP with 10% FO_8T_8

103°



AFEP with 10% FD_8T_8

Water Contact Angle

Polymer	No POSS	FO_8T_8	FD_8T_8
PCTFE	88°	108°	128°
FEP	97°	110°	114°
Amor. FEP	92°	100°	103°

Fluoropropyl POSS (FP_nT_n)	101°
Fluorooctyl POSS (FO_8T_8)	115°
Fluorodecyl POSS (FD_8T_8)	154°

Summary

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SEM Images	Marietta Fernandez
SEM Images	Erik Weber
AFM Images	Brian Moore

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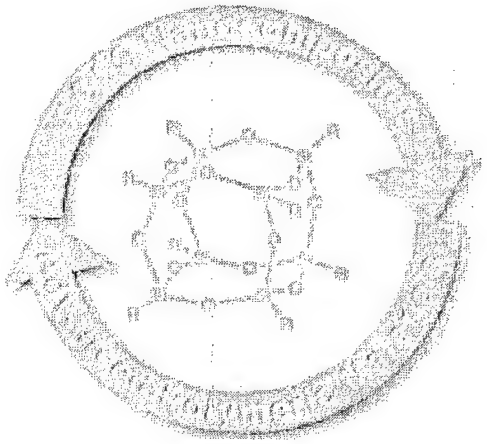
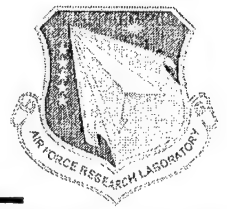
Dr. Sandra Tomczak
Mr. Brian Moore
Dr. Brent Viers
Dr. Darrell Marchant
Lt Will Cooper
Mr. Scott Barker



Dr. Shawn Phillips
Lt Amy Palacek
Dr. Rusty Blanski
Dr. Joe Mabry
Mrs. Sherly Largo
Dr. Tim Haddad
Lt Laura Moody

Financial Support:
Air Force Office of Scientific Research
Air Force Research Laboratory, Propulsion Directorate



Backup Slides

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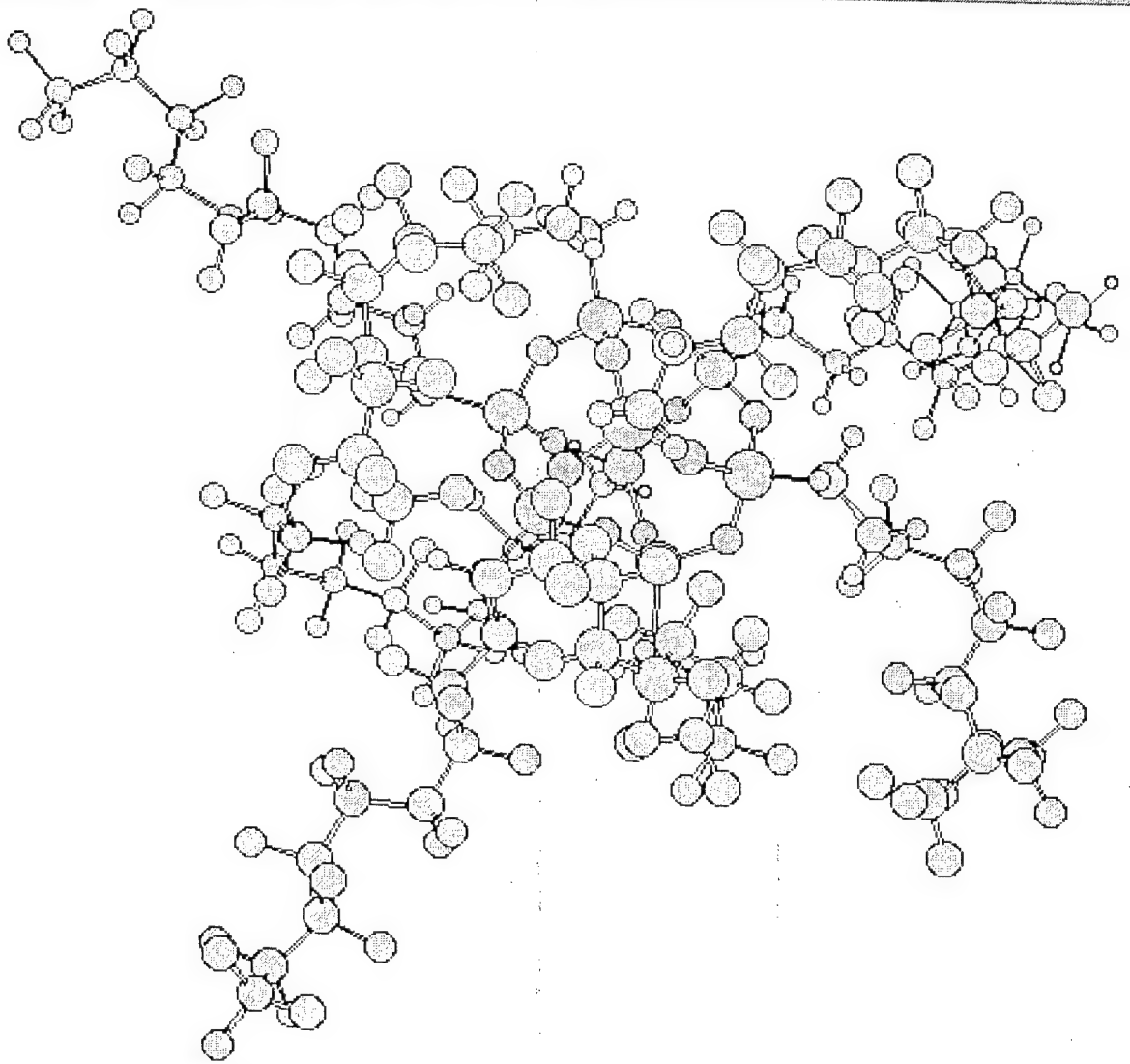
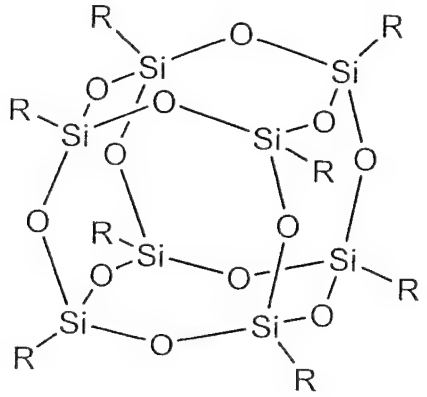
Gas Phase Model of Fluorodecyl$_8$T$_8$



Density

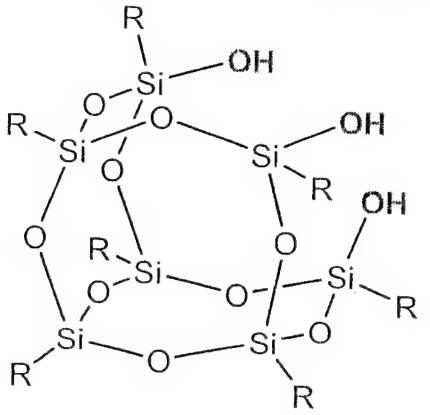
Compound	Density (g/mL)
• PVDF	1.75-1.78
• PCTFE	2.08-2.19
• FEP	2.12-2.17
• Fluoropropyl POSS	1.59
• Fluorohexyl POSS (crystal)	1.86 (1.98)
• Fluorooctyl POSS (crystal)	1.88 (2.05)
• Fluorodecyl POSS (crystal)	1.95 (2.06)

Fluorinated POSS Trisilanol

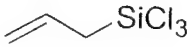


Et_4NOH

reflux

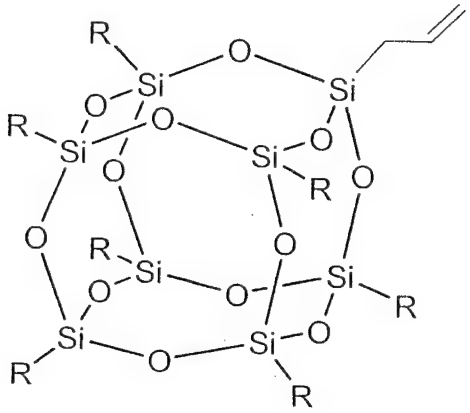


Et_3N

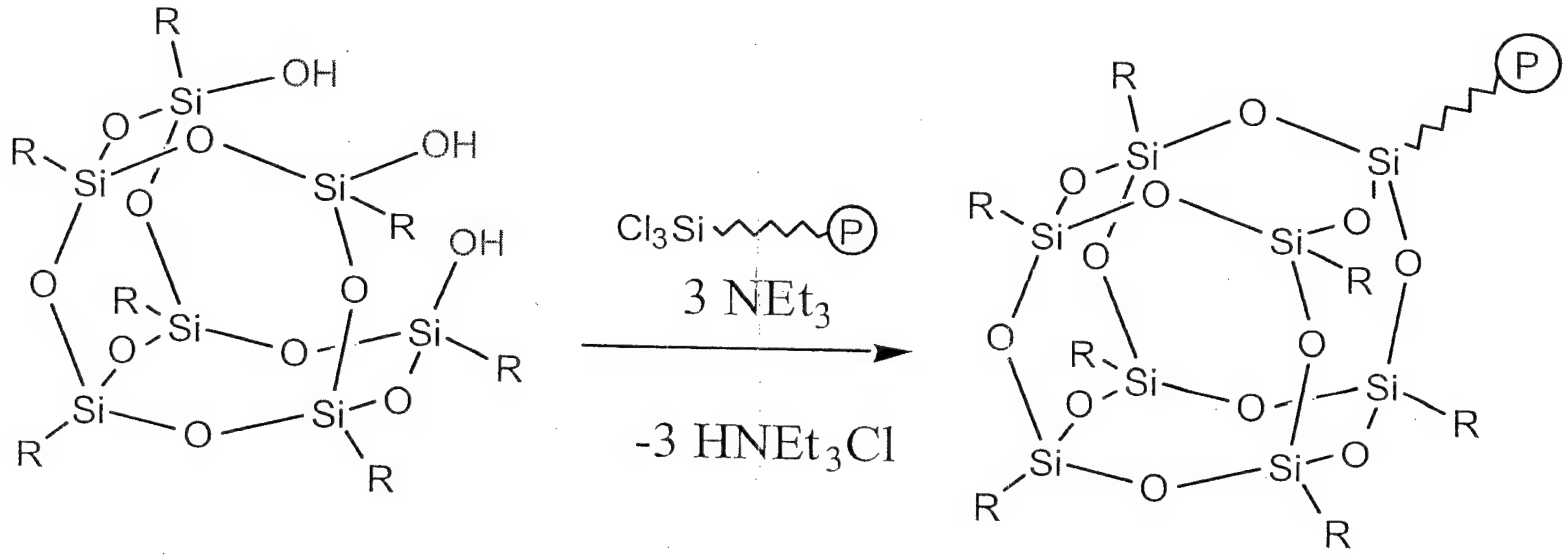


$SiCl_3$

(or other chlorosilanes)



POSS Macromers for Nanocomposites



POSS-based macromers are available through either **Gelest** or **Aldrich**
POSS technology is commercialized by **Hybrid Plastics** in Fountain Valley CA

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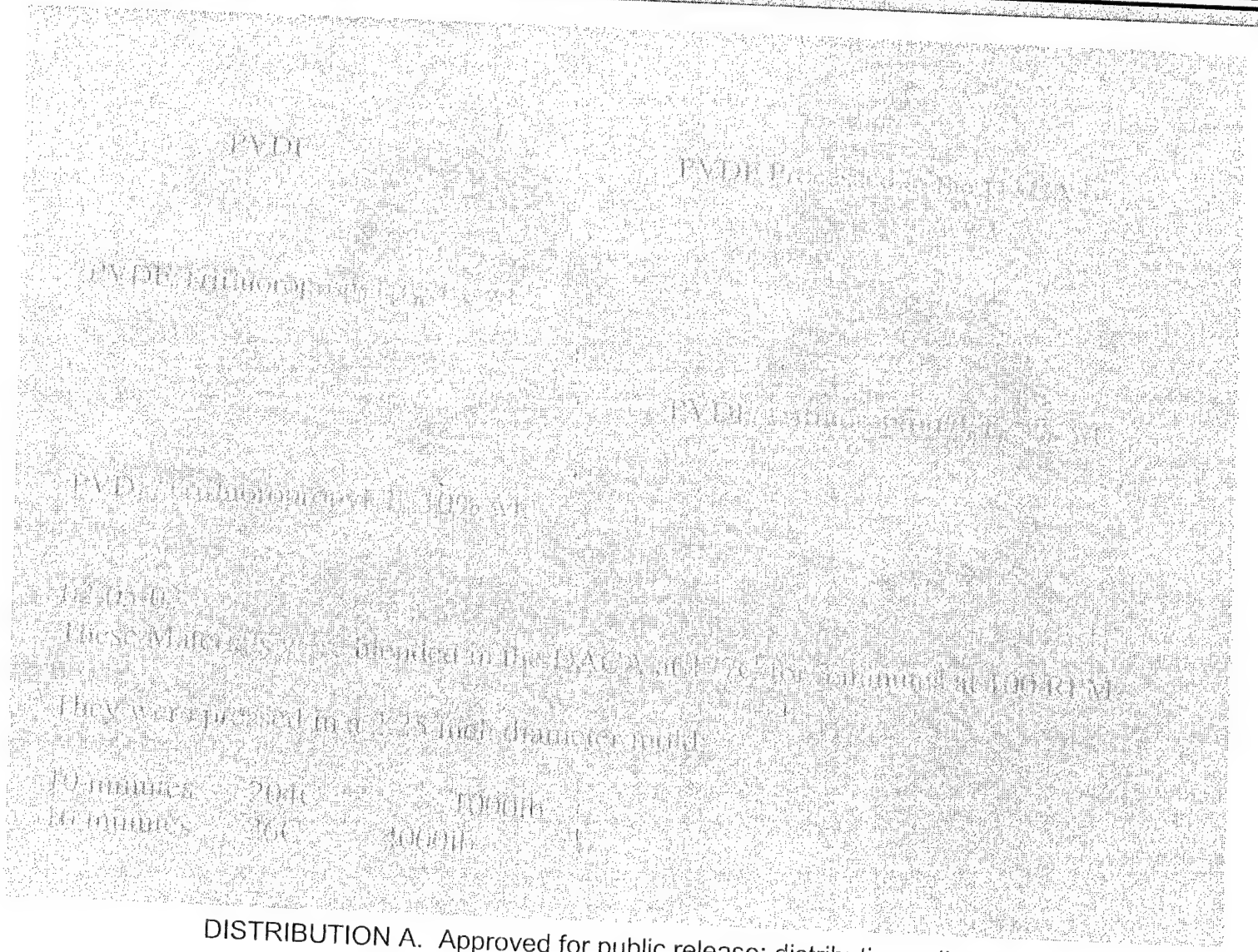
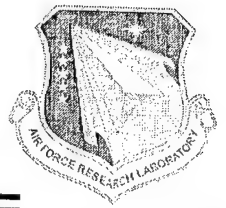
PVDF Fluoropropyl$_n$T$_n$ Blends





POSS Siloxanes

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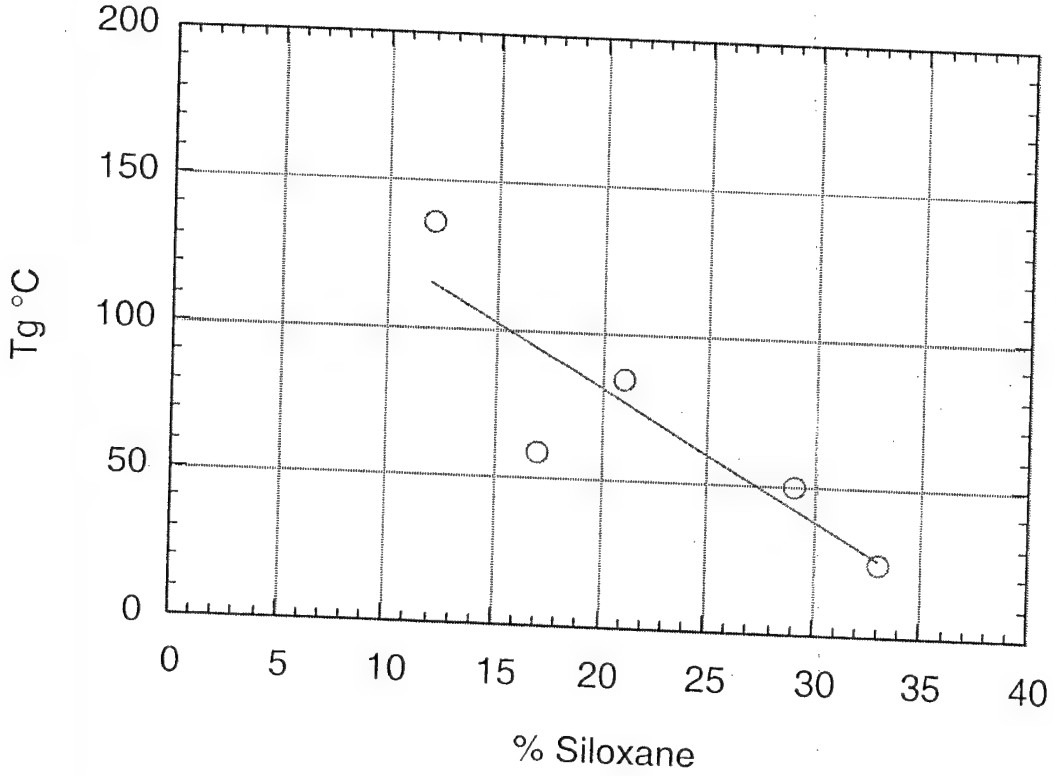
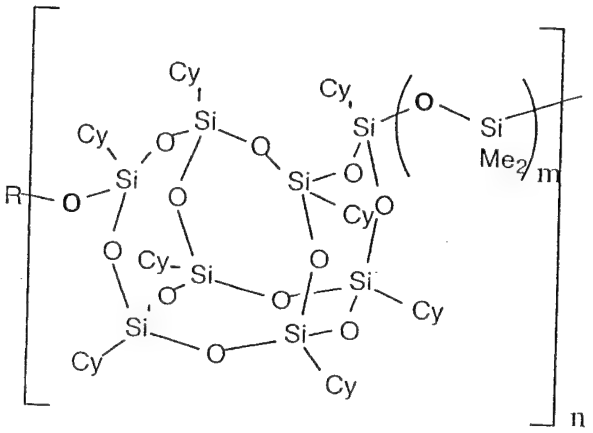
Tg's For Bead Siloxane Copolymers





POSS Bead acts as a hard segment

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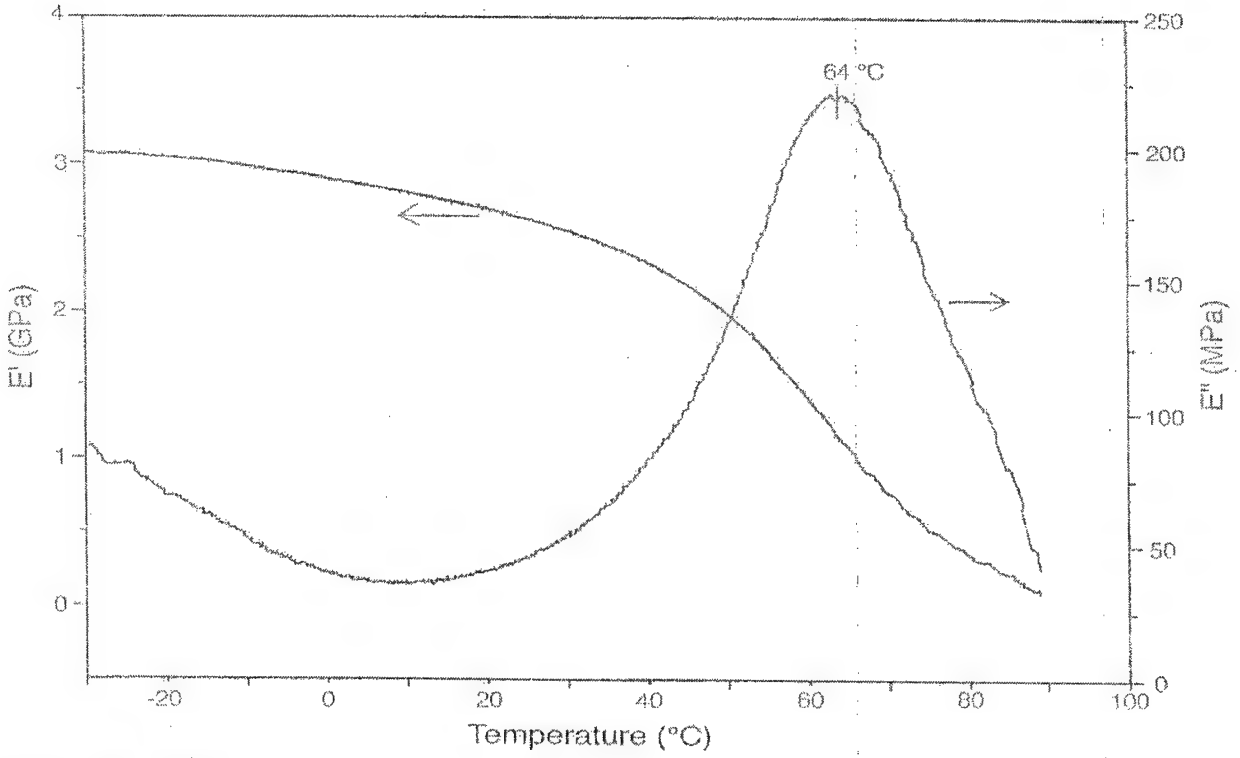
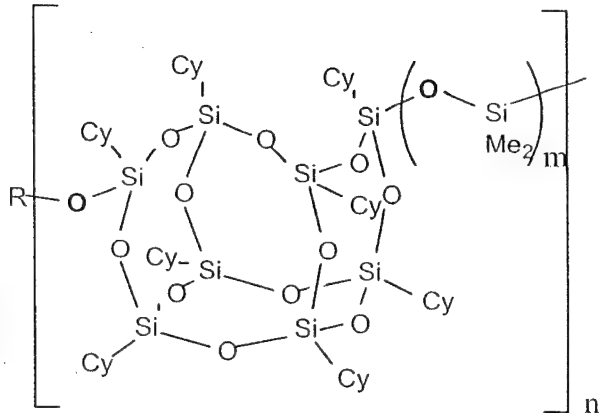
POSS Siloxanes

- Copolymers with low softening temperatures can be molded into bars.
- Dynamic mechanical analysis reveals a T_g (64°C).





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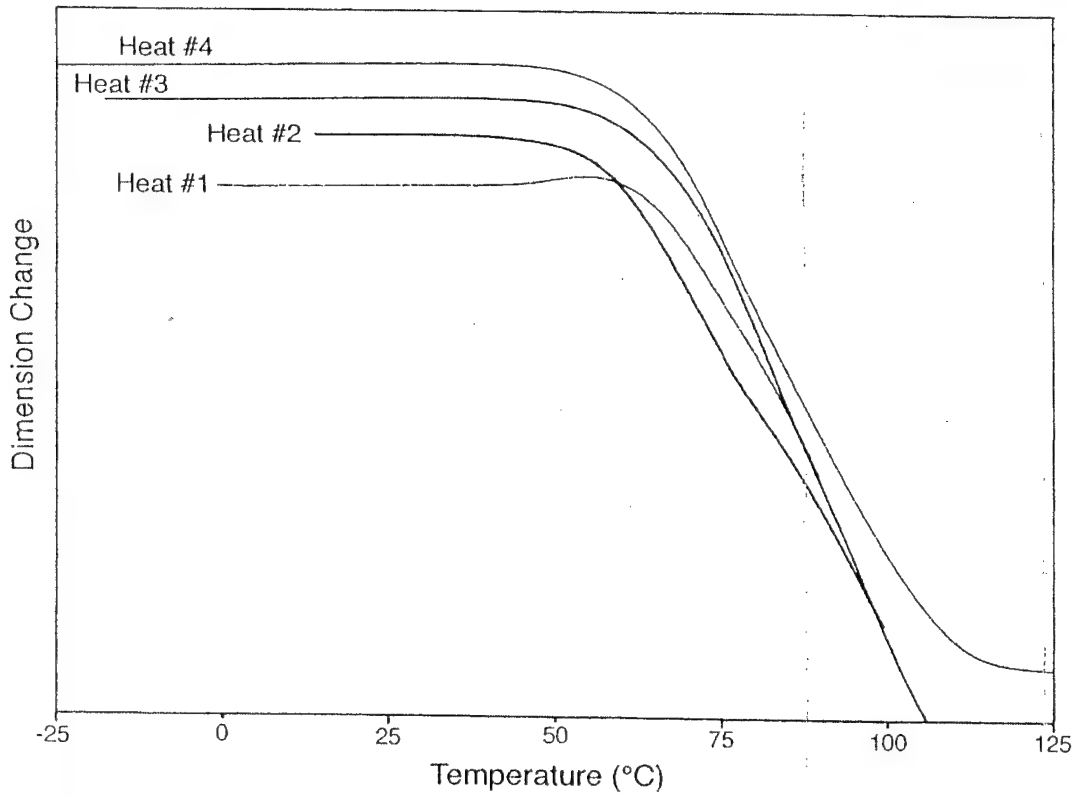
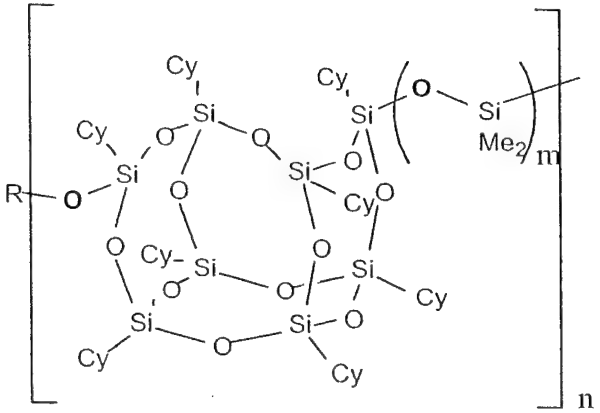
POSS Siloxanes

The POSS/Siloxane copolymers with four or more Si-O repeat units in the siloxane segment have softening temperatures well below the decomposition temperatures.





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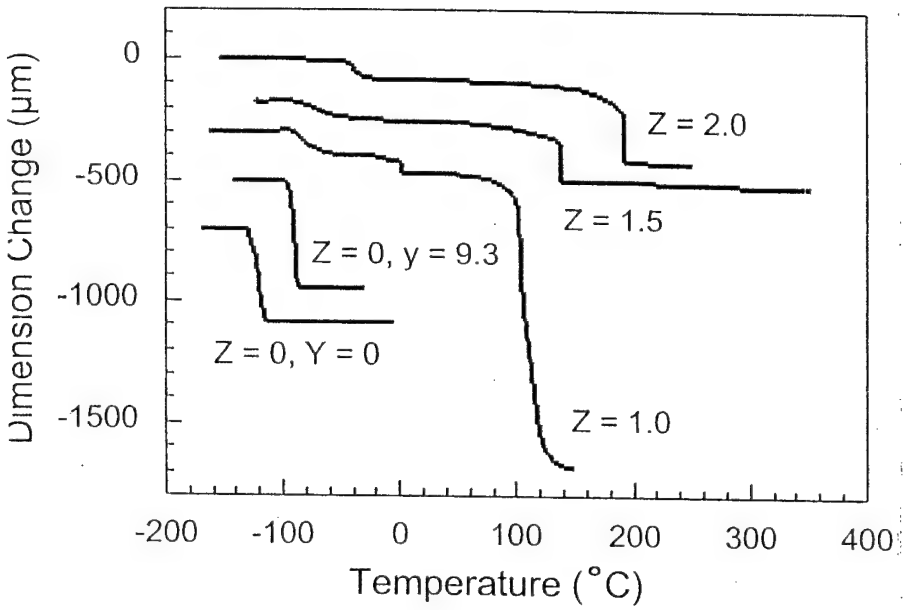
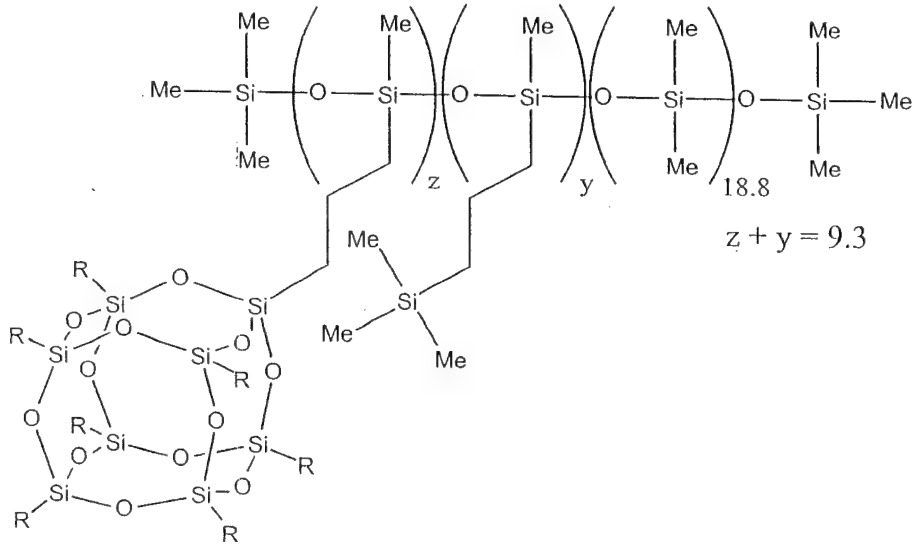
TMA of Pendent POSS-Siloxanes





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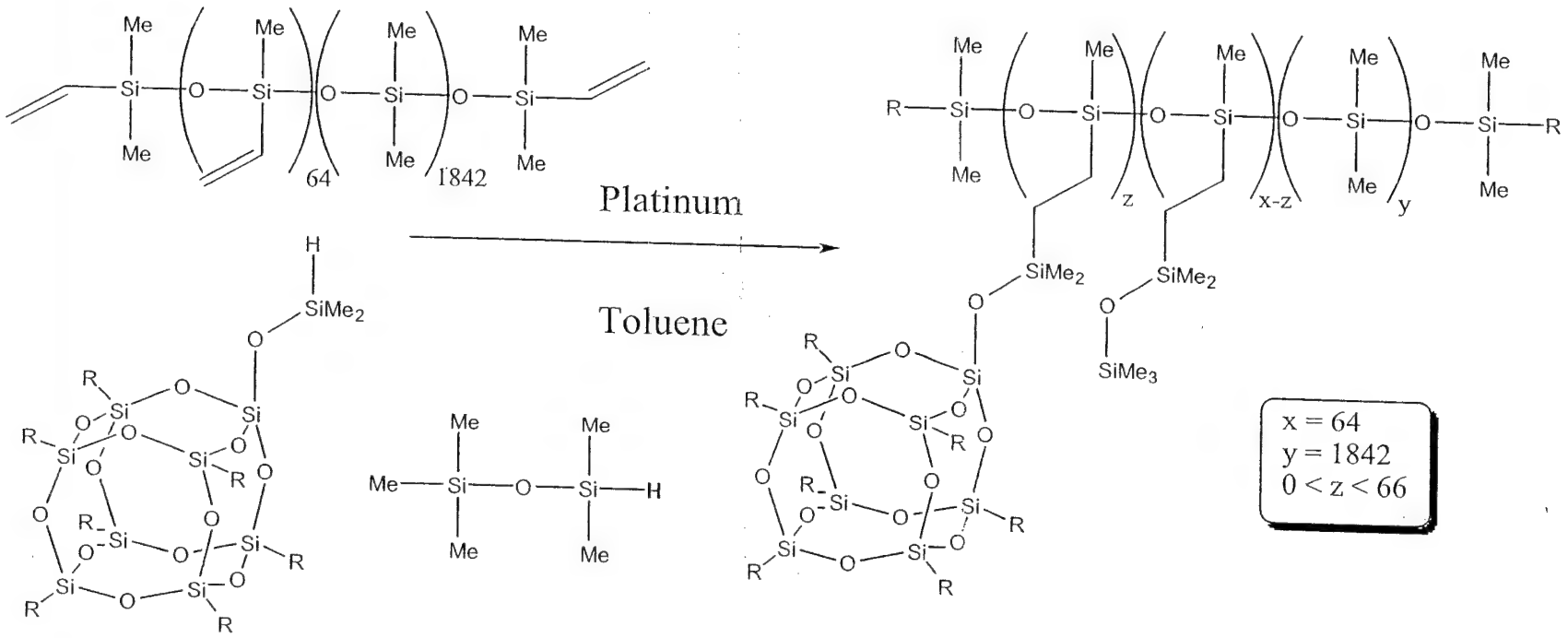
Hydrosilation to High MW PDMS



Used 5 weight % POSS

There are about 7 POSS-macromers per PDMS chain

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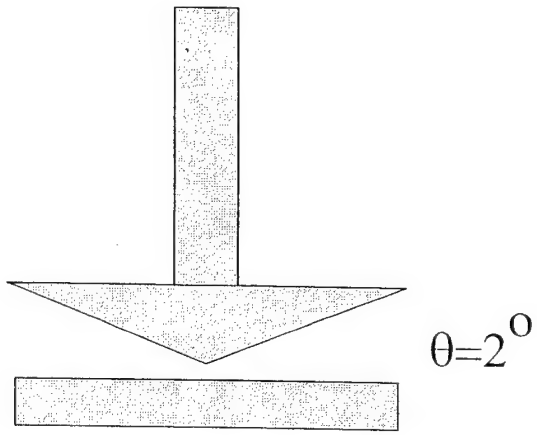
Experimental Setup for Rheology

$$\gamma(\omega)=\gamma_o \sin(\omega t)$$

$$\omega=2\pi\ (\sec^{-1})$$

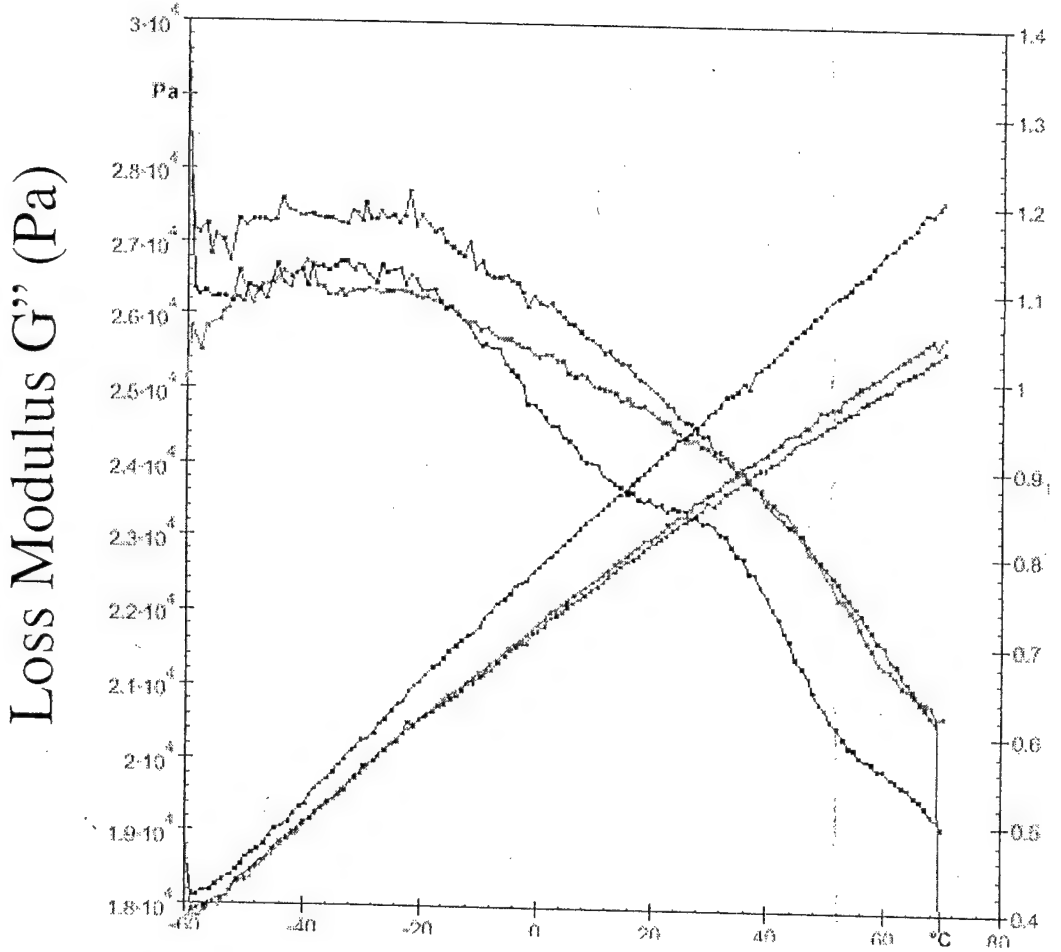


- 25 mm diameter cone-and plate with cone angle of 2° was used.
- The strain amplitude γ_o is 1% and angular frequency ω is 2π per second.
- The temperature is ramped from -60°C to 70°C with a rate of 2°C/min.

The loss modulus G" and $\tan\delta$ =G"/G' were obtained as a function of temperature.

Andre Lee, AFRL

Comparison of Three T8-POSS Macromers

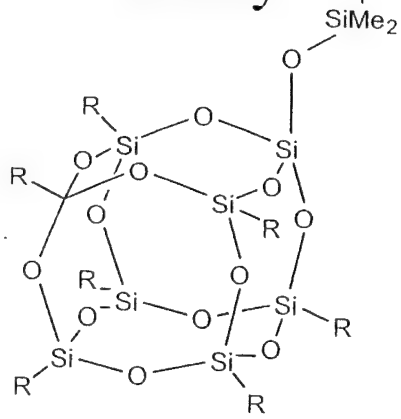


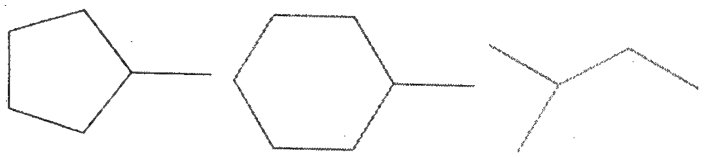
PDMS + 5 wt % POSS

Blue = cyclopentyl

Red = cyclohexyl

Purple = isobutyl





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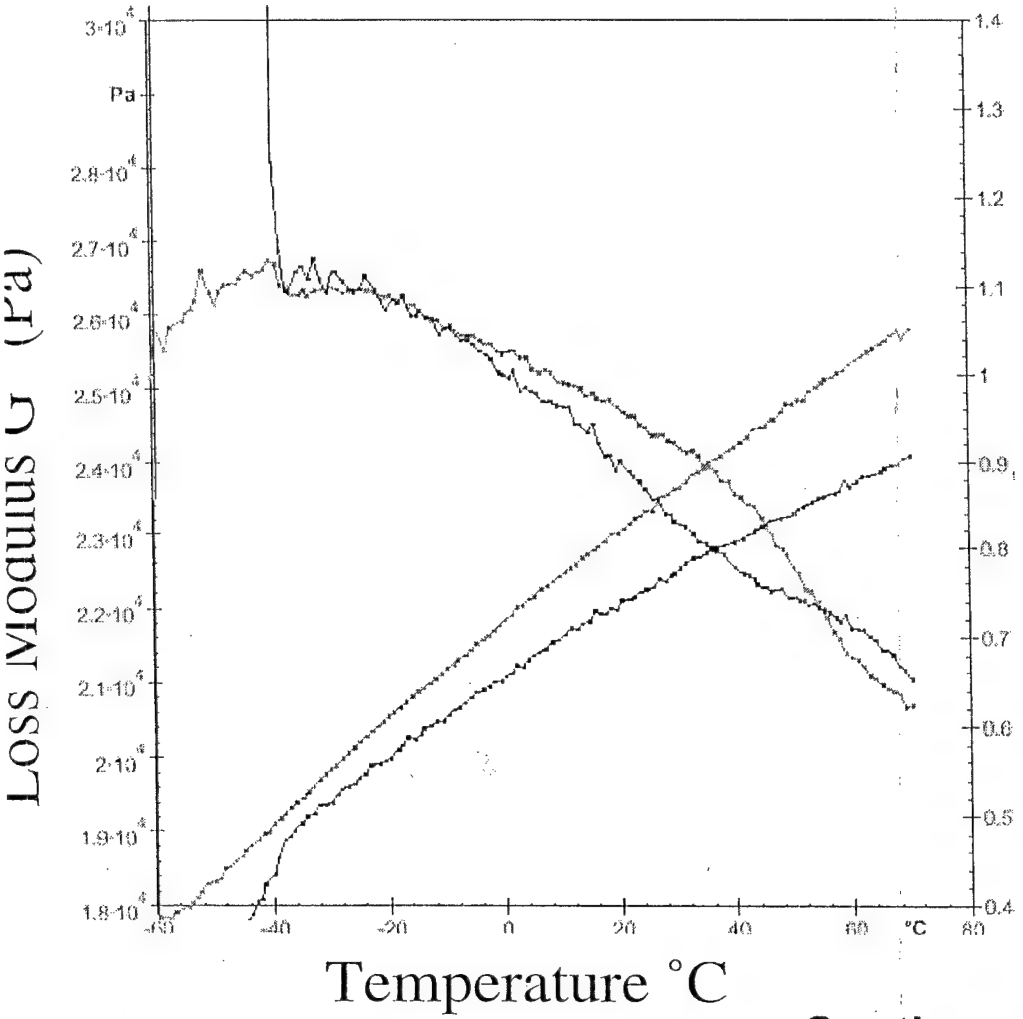
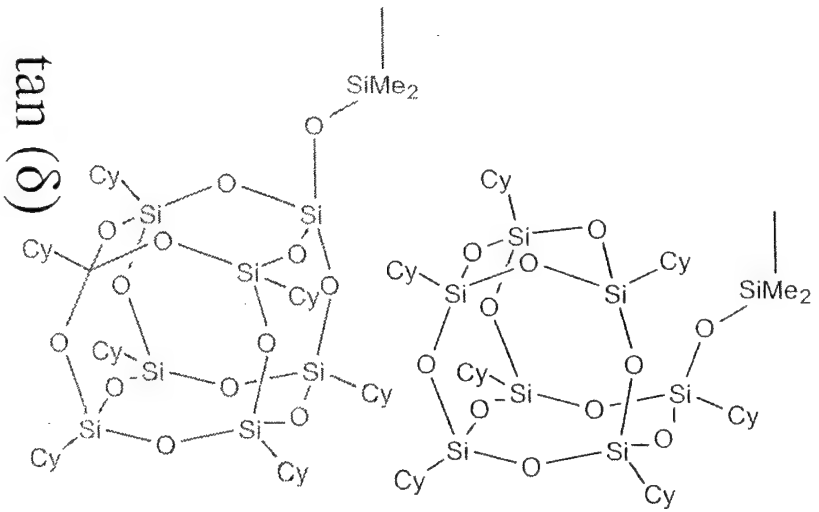
Andre Lee, AFRL

Comparison of Two POSS Polyhedra



PDMS + 5 wt %
CyclohexylPOSS
Red = T8-POSS
Blue = T7-POSS



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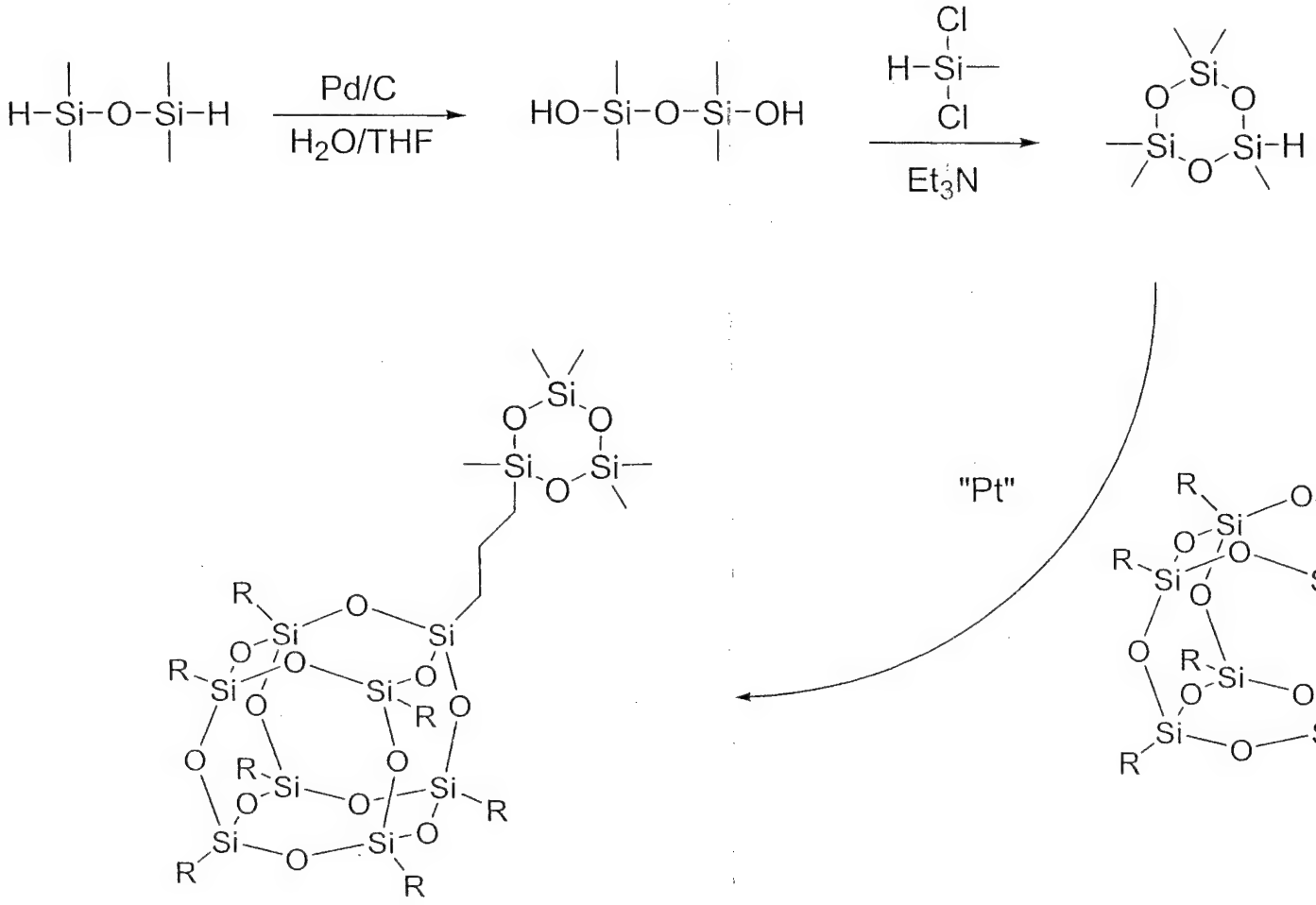
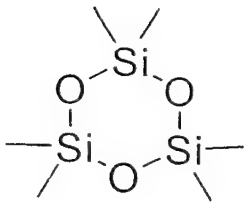
Continue this collaboration with Andre Lee

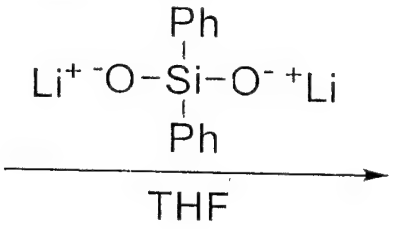
POSS Cyclotrisiloxane

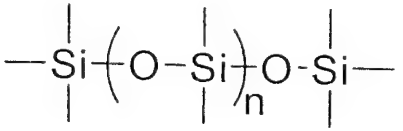


Reactivity

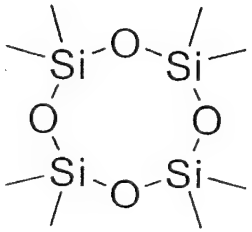


D_3

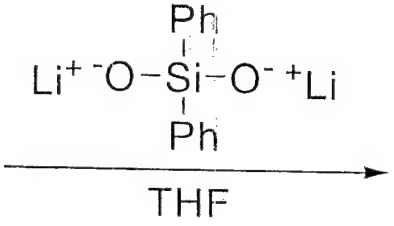




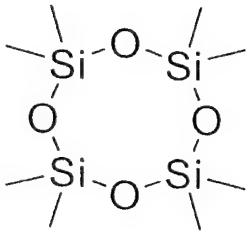
PDMS



D_4



No Reaction



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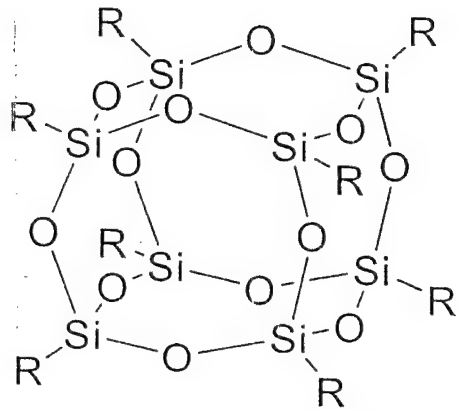
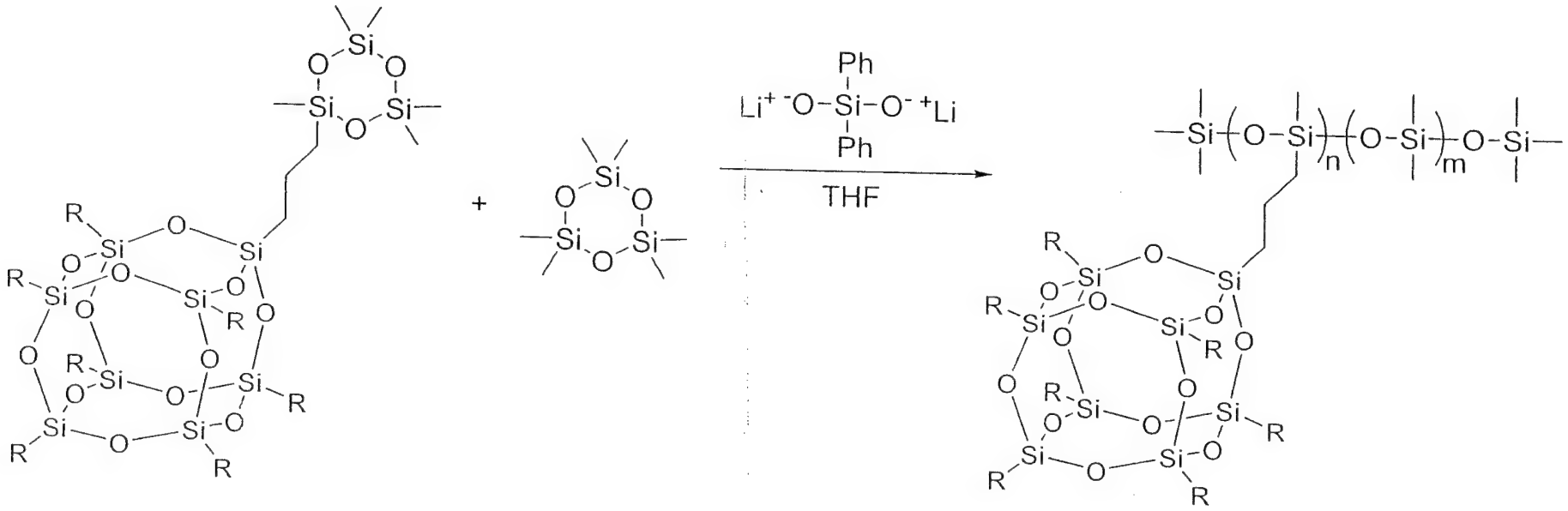
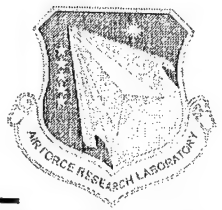


DISTRIBUTION A. Approved for public release; distribution unlimited.

POSS Siloxane Copolymers

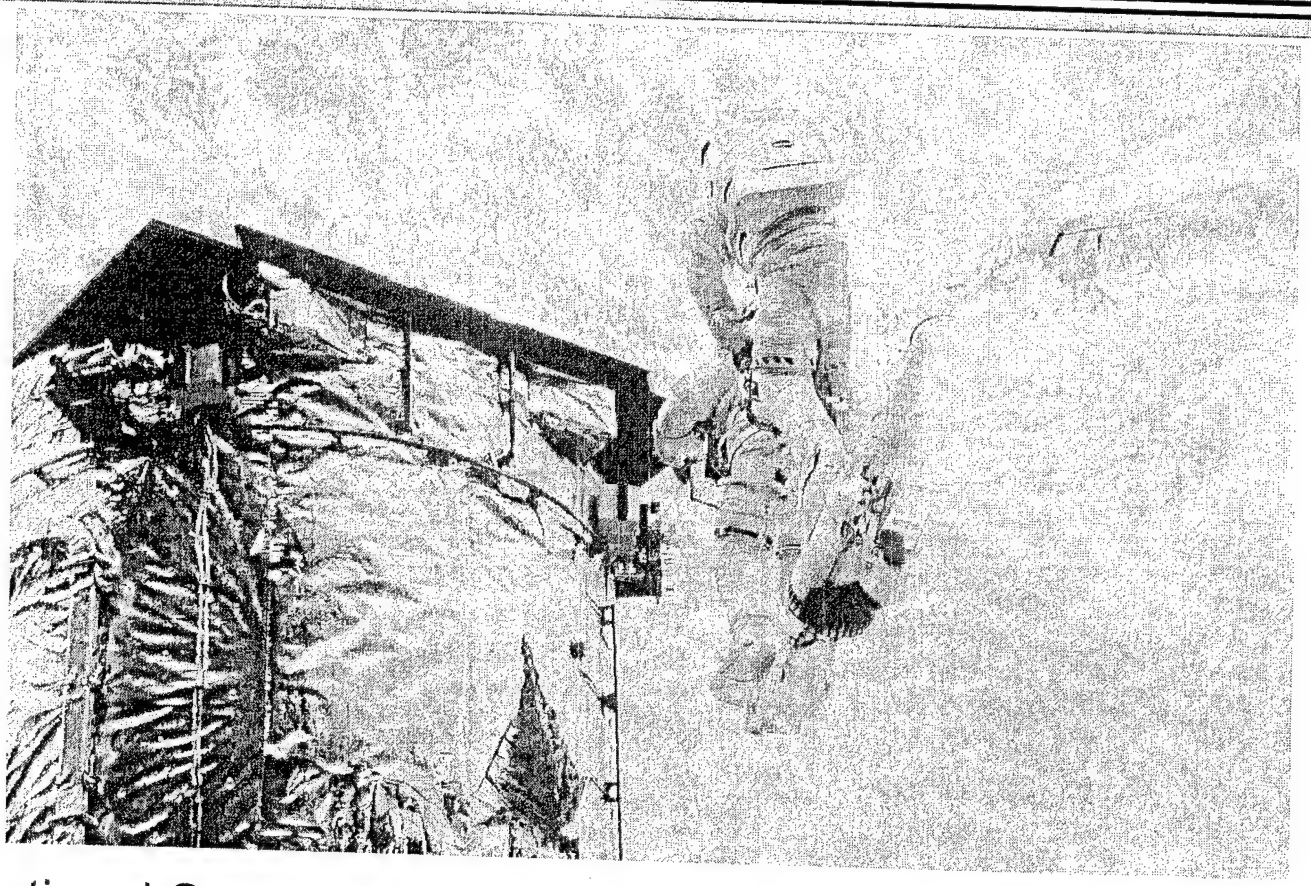




Space-Survivable Materials

PAS-03-061

Space Materials

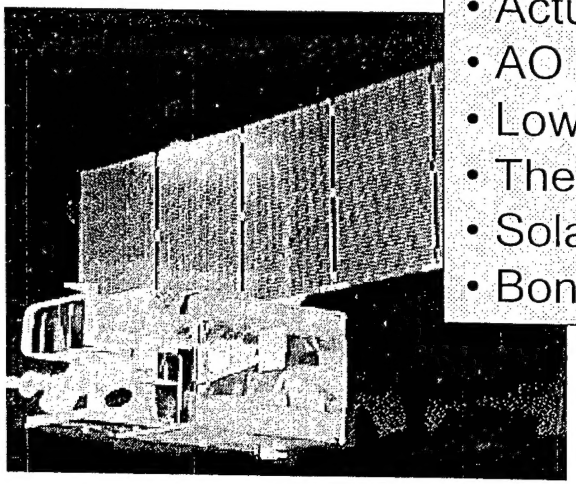


- The International Space Station, the Space Shuttle, and the Hubble Space Telescope are among satellites that operate in Low Earth Orbit (LEO)
- Metallized Teflon FEP is commonly used as outer layer of multi-layer insulation.

Space-Survivable Polymers

LEO Environment (Altitudes of 200 to 1500 km)

- Atomic Oxygen (AO): ~10^8 atoms/cm^3
- Actual AO flux on spacecraft ~10^{15} atoms/cm^2•s
- AO Collision energy ~ **5eV (7.8 km/sec)**
- Low-energy and high energy charged particles.
- Thermal cycling -50 to 150°C
- Solar VUV and UV radiation (~ 150 – 400 nm).
- Bond scission and radical formation can lead to embrittlement.



Satellites & Space Systems

Bond	Dissociation Energy (eV)	λ (nm)	Material
CF_2-CF_2	4.3	290	FEP Teflon®
CF_2-F	5.5	230	FEP Teflon®
Si-O	8.3	150	Nanocomposite

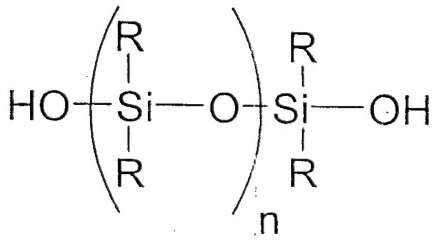
Objectives

- **Increase space-survivability of polymeric materials**
- **Develop self-passivating layer based on nanocomposite incorporation**

Siloxanes

Siloxanes systems exhibit superior resistance to AO

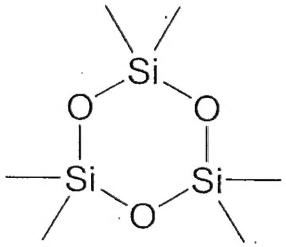
- **High Si-O bond strength ~ 8 eV**



R = CH_3,

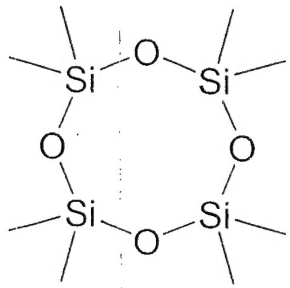
However, pure siloxane systems have disadvantages

- **Volatile cyclic species which recondense on optical surfaces**



Cyclo($Me_2SiO)_3$

(D_3)



Cyclo($Me_2SiO)_4$

(D_4)

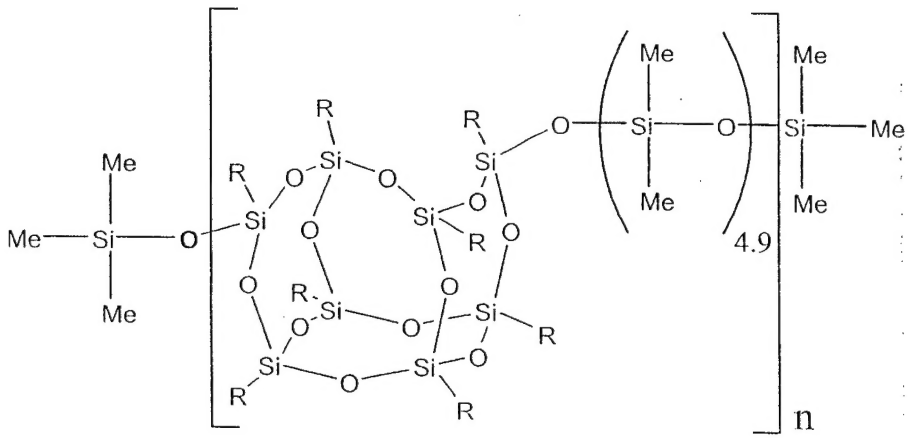
Cyclo($Me_2SiO)_5$ (D_5)

Cyclo($Me_2SiO)_6$ (D_6)

Cyclo($Me_2SiO)_7$ (D_7)

POSS-Siloxane

After AO exposure, POSS siloxane had no erosion



Composition, at %

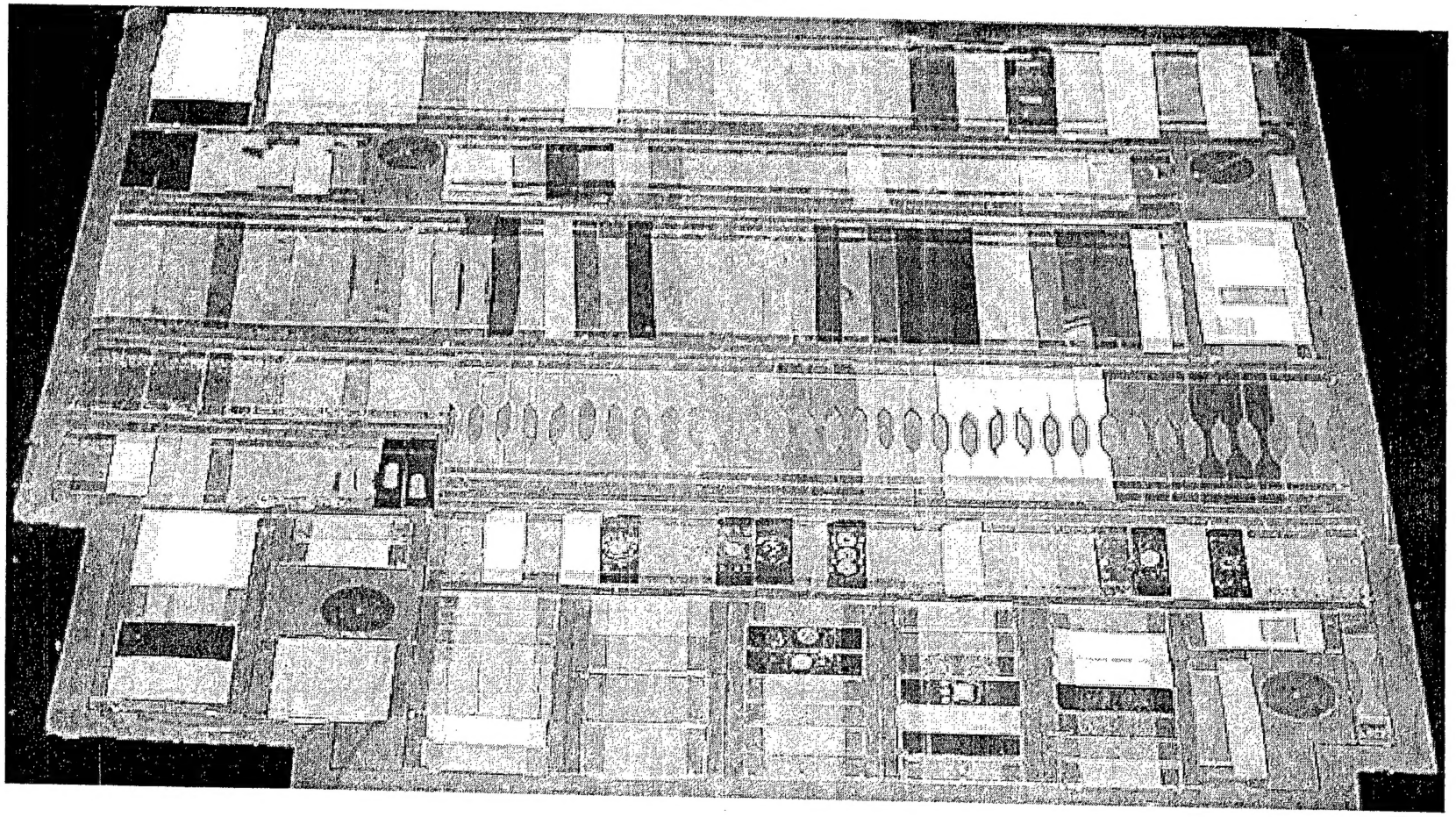
Sample Treatment	C	O	Si
As entered	65.0	18.5	16.6
2.0 hr	48.4	33.8	17.8
24.6 hr	22.1	49.1	28.8
63.0 hr	16.3	55.7	28.0
4.8 hr air	19.5	52.8	27.7

Gonzalez, R. I., Phillips, S. H., Hoflund, G. B., *J. of Spacecraft and Rockets*, Vol 37, No. 4, **2000**, pp. 463-467.

XPS survey spectra obtained from a solvent-cleaned, POSS-PDMS film.

Materials International Space Station Experiment (MISSE)

MISSE 5



Pictures courtesy of NASA